

-71-

1 this method. Thus, the amounts of polymer, transition metal catalyst and any
2 photoinitiator, antioxidant, polymeric diluents and additives, can vary
3 depending on the article and its end use.

4 For instance, one of the primary functions of the polymer described above is
5 to react irreversibly with oxygen during the scavenging process, while the
6 primary function of the transition metal catalyst is to facilitate this process.
7 Thus, to a large extent, the amount of polymer present will affect the oxygen
8 scavenging capacity of the composition, i.e., affect the amount of oxygen that
9 the composition can consume. The amount of transition metal catalyst will
10 affect the rate at which oxygen is consumed. Because it primarily affects the
11 scavenging rate, the amount of transition metal catalyst may also affect the
12 onset of oxygen scavenging (induction period).

13 It has been found that the subject polymers, when used as part of the present
14 composition, provide oxygen scavenger properties at desirable rate and
15 capacity while causing the composition to have enhanced processability and
16 compatibility properties over conventional ethylenically unsaturated polymers.
17 Thus, the present composition can be used to provide, by itself or as a blend
18 with diluent polymers, such as polyolefins and the like, a packaging material
19 or film having enhanced processability properties. Further, the present
20 composition consumes and depletes the oxygen within a package cavity
21 without substantially detracting from the color, taste and/or odor of the
22 product contained within the package cavity.

23 The amount of the above-described polymer contained as part of the present
24 composition may range from about 1 to 100% by weight of the composition or
25 layer composed of said composition in which both polymer and transition
26 metal catalyst are present (hereinafter referred to as the "scavenging
27 composition", e.g., in a coextruded film or container, the scavenging
28 composition would comprise the particular layer(s) in which both the

-72-

1 copolymer and transition metal catalyst components are present together).
2 Typically, the amount of transition metal catalyst may range from 0.001 to 1%
3 (10 to 10,000 ppm) of the scavenging composition, based on the metal
4 content only (excluding ligands, counterions, etc.). In the event the amount of
5 transition metal catalyst is less than 1%, it follows that the polymer and any
6 additives will comprise substantially all of the remainder of the composition.
7 The polymer of the present invention may further be combined with other
8 polymeric oxygen scavenger agents.

9 Any further additives employed normally will not comprise more than 10% of
10 the scavenging composition, with preferable amounts being less than 5% by
11 weight of the scavenging composition.

12 Optionally, the compositions and process of this invention can include
13 exposure of the polymer containing the oxygen scavenging-promoting
14 transition metal to actinic radiation to reduce the induction period, if any,
15 before oxygen scavenging commences. A method is known for initiating
16 oxygen scavenging by exposing a film comprising an oxidizable organic
17 compound and a transition metal catalyst to actinic radiation. A composition
18 of the present invention which has a long induction period in the absence of
19 actinic radiation but a short or non-existent induction period after exposure to
20 actinic radiation is particularly preferred. They maintain a high capability for
21 scavenging oxygen upon activation with actinic radiation. Thus, oxygen
22 scavenging can be activated when desired.

23 The radiation used in this method should be actinic, e.g., ultraviolet or visible
24 light having a wavelength of about 200 to 750 nanometers (nm), and
25 preferably having a wavelength of about 200 to 600 nm, and most preferably
26 from about 200 to 400 nm. When employing this method, it is preferable to
27 expose the oxygen scavenger to at least 0.01 Joule per gram of scavenging
28 composition. A typical amount of exposure is in the range of 10 to

1 2000 Joules per gram. The radiation can also be an electron beam radiation
2 at a dosage of about 2 to 200 kiloGray, preferably about 10 to 100 kiloGray.
3 Other sources of radiation include ionizing radiation such as gamma, X-rays
4 and corona discharge. The duration of exposure depends on several factors
5 including, but not limited to, the amount and type of photoinitiator present,
6 thickness of the layers to be exposed, thickness and opacity of intervening
7 layers amount of any antioxidant present, and the wavelength and intensity of
8 the radiation source. The radiation provided by heating of polyolefin and the
9 like polymers (e.g., 100-250°C) during processing does not cause triggering.

10 Oxygen-scavenging compositions of the present invention are useful in many
11 ways. The compositions can be dispersed as small particles for absorbing
12 oxygen or can be coated onto materials such as metallic foil, polymer film,
13 metalized film, paper or cardboard to provide, in some embodiments,
14 scavenging properties and/or adhesive properties. The compositions are also
15 useful in making articles such as single or multi-layer rigid thick-walled plastic
16 containers or bottles (typically, between 5 and 100 mils in thickness) or in
17 making single or multi-layer flexible films, especially thin films (less than
18 5 mils, or even as thin as about 0.25 mil). Some of the compositions of the
19 present invention are easily formed into films using well-known means.
20 These films can be used alone or in combination with other films or materials.

21 The compositions of the present invention may be further combined with one
22 or more polymers, such as thermoplastic polymers which are typically used to
23 form film layers in plastic packaging articles. In the manufacture of certain
24 packaging articles, well-known thermosets can also be used as a polymeric
25 diluent.

26 Selecting combinations of a diluent and the composition of the present
27 invention depends on the properties desired. Polymers which can be used as
28 the diluent include, but are not limited to, polyethylene, low or very low density

-74-

1 polyethylene, polypropylene, polyvinyl chloride, and ethylene copolymers
2 such as ethylene-vinyl acetate, ethylene-alkyl acrylates or methacrylates,
3 ethylene-acrylic acid or methacrylic acid, and ethylene-arylic or metharylic
4 acid ionomers. In rigid packaging applications, polystyrene is often used.
5 Blends of different diluents may also be used. However, as indicated above,
6 the selection of the polymeric diluent largely depends on the article to be
7 manufactured and the end use. Such selection factors are well known in the
8 art.

9 If a diluent polymer such as a thermoplastic is employed, it should further be
10 selected according to its compatibility with the composition of the present
11 invention. In some instances, the clarity, cleanliness, effectiveness as an
12 oxygen-scavenger, barrier properties, mechanical properties and/or texture of
13 the article can be adversely affected by a blend containing a polymer which is
14 incompatible with the composition of the present invention.

15 A blend of a composition of the present invention with a compatible polymer
16 can be made by dry blending or by melt-blending the polymers together at a
17 temperature in the approximate range of 50°C to 250°C. Alternative methods
18 of blending include the use of a solvent followed by evaporation. When
19 making film layers or articles from oxygen-scavenging compositions, extrusion
20 or coextrusion, solvent casting, injection molding, stretch blow molding,
21 orientation, thermoforming, extrusion coating, coating and curing, lamination
22 or combinations thereof would typically follow the blending.

23 Layers comprising the composition of the present invention may be in several
24 forms. They may be in the form of stock films, including "oriented" or "heat
25 shrinkable" films, which may ultimately be processed as bags, etc., or in the
26 form of stretch-wrap films. The layers may also be in the form of sheet inserts
27 to be placed in a packaging cavity. In rigid articles such as beverage
28 containers, thermoformed trays or cups, the layer may be within the

1 container's walls. Even further, the layer may also be in the form of a liner
2 placed with or in the container's lid or cap. The layer may even be coated or
3 laminated onto any one of the articles mentioned above.

4 In multi-layered articles, the scavenging layer comprising the composition of
5 the present invention may be included with layers such as, but not necessarily
6 limited to, "oxygen barriers", i.e., layers of material having an oxygen
7 transmission rate equal to or less than 100 cubic centimeters-mil per square
8 meter (cc-mil/m²) per day per atmosphere pressure at room temperature, i.e.,
9 about 25°C. Typical oxygen barriers comprise poly(ethylene vinyl alcohol),
10 polyacrylonitrile, polyvinyl chloride, poly(vinylidene dichloride), polyethylene
11 terephthalate, silica and polyamides. Metal foil layers can also be employed.

12 Other additional layers may include one or more layers which are permeable
13 to oxygen. In one preferred packaging construction, especially for flexible
14 packaging for food, the layers include, in order starting from the outside of the
15 package to the innermost layer of the package, (i) an oxygen barrier layer,
16 (ii) a scavenging layer, i.e., the scavenging composition as defined earlier,
17 and, optionally, (iii) an oxygen permeable layer. Control of the oxygen barrier
18 property of (i) allows a means to regulate the scavenging life of the package
19 by limiting the rate of oxygen entry to the scavenging composition (ii), and
20 thus limiting the rate of consumption of scavenging capacity. Control of the
21 oxygen permeability of layer (iii) allows a means to set an upper limit on the
22 rate of oxygen scavenging for the overall structure independent of the
23 composition of the scavenging composition (ii). This can serve the purpose of
24 extending the handling lifetime of the films in the presence of air prior to
25 sealing of the package. Furthermore, layer (iii) can provide a barrier to
26 migration of the individual components in the scavenging films or by-products
27 of scavenging into the package interior. Even further, layer (iii) also improves
28 the heat-sealability, clarity and/or resistance to blocking of the multi-layer film.

-76-

1 Further, additional layers such as adhesive layers may also be used.
2 Compositions typically used for adhesive layers include anhydride functional
3 polyolefins and other well-known adhesive layers.

4 To determine the oxygen scavenging capabilities of a composition, the rate of
5 oxygen scavenging can be calculated by measuring the time that elapsed
6 before the article depletes a certain amount of oxygen from a sealed
7 container. For instance, a film comprising the scavenging component can be
8 placed in an air-tight, sealed container of a certain oxygen containing
9 atmosphere, e.g., air which typically contains 20.9% oxygen by volume.
10 Then, over a period of time, samples of the atmosphere inside the container
11 are removed to determine the percentage of oxygen remaining. The
12 scavenging rates of the composition and layers of the present invention will
13 change with changing temperature and atmospheric conditions.

14 When an active oxygen barrier is prepared, the scavenging rate can be as
15 low as 0.1 cc oxygen per gram of composition of the present invention per
16 day in air at 25°C and a 1 atmosphere pressure. However, preferable
17 compositions of this invention have rates equal to or greater than 1 cc oxygen
18 per gram per day, thus making them suitable for scavenging oxygen from
19 within a package, as well as suitable for active oxygen barrier applications.
20 Many compositions are even capable of more preferable rates equal to or
21 greater than 5.0 cc O₂ per gram per day.

22 Generally, film layers suitable for use as an active oxygen barrier can have an
23 oxygen transmission rate as high as 10 cc oxygen per square meter per mil
24 per day when measured in air at 25°C and 1 atmosphere pressure.
25 Preferably, a layer of this invention has an oxygen transmission rate less than
26 about 1 cc oxygen per square meter per mil per day, and more preferably has
27 an oxygen transmission rate less than about 0.2 cc oxygen per square meter
28 per rail per day under the same conditions, thus making it suitable for active

-77-

1 oxygen barrier applications as well as for scavenging oxygen from within a
2 package.

3 In an active oxygen barrier application, it is preferable that the combination of
4 oxygen barriers and any oxygen scavenging activity create an overall oxygen
5 transmission rate of less than about 1.0 cubic centimeter-mil per square
6 meter per day per atmosphere pressure at 25°C. Another definition of
7 acceptable oxygen scavenging is derived from testing actual packages. In
8 actual use, the scavenging rate requirement will largely depend on the
9 internal atmosphere of the package, the contents of the package and the
10 temperature at which it is stored.

11 In a packaging article made according to this invention, the scavenging rate
12 will depend primarily on the amount and nature of the composition of the
13 present invention in the article, and secondarily on the amount and nature of
14 other additives (e.g., diluent polymer, antioxidant, etc.) which are present in
15 the scavenging component, as well as the overall manner in which the
16 package is fabricated, e.g., surface area/volume ratio.

17 The oxygen scavenging capacity of an article comprising the invention can be
18 measured by determining the amount of oxygen consumed until the article
19 becomes ineffective as a scavenger. The scavenging capacity of the
20 package will depend primarily on the amount and nature of the scavenging
21 moieties present in the article, as discussed above.

22 In actual use, the oxygen scavenging capacity requirement of the article will
23 largely depend on three parameters of each application:

24 (1) the quantity of oxygen initially present in the package;

-78-

1 (2) the rate of oxygen entry into the package in the absence of the
2 scavenging property; and

3 (3) the intended shelf life for the package.

4 The scavenging capacity of the composition can be as low as 1 cc oxygen per
5 gram, but is preferably at least 10 cc oxygen per gram, and more preferably
6 at least 50 cc oxygen per gram. When such compositions are in a layer, the
7 layer will preferably have an oxygen capacity of at least 250 cc oxygen per
8 square meter per mil thickness and more preferably at least 500 cc oxygen
9 per square meter per mil thickness.

10 Other factors may also affect oxygen scavenging and should be considered
11 when selecting compositions. These factors include but are not limited to
12 temperature, relative humidity, and the atmospheric environment in the
13 package.

14 Applicants have achieved a composition for a rigid beverage and food
15 container comprising PET and/or PEN, the container incorporating an oxygen
16 scavenging component of cyclic olefin which oxidizes oxygen in the interior of
17 the container without giving off odor and/or taste as a result of its oxygen
18 scavenging function, nor does it cause a change in molecular weight. This is
19 because the cyclic olefin oxygen scavenging component does not fragment
20 as it oxidizes, Thus the composition maintains the structural integrity of the
21 container while avoiding the problem of imparting oxidation byproducts to the
22 packaged material.

23

24 EXAMPLES

25 Objects and advantages of this invention are further illustrated by the
26 following examples. The particular materials and amounts thereof, as well as

-79-

1 other conditions and details, recited in these examples should not be used to
2 unduly limit this invention.

3

4 Example 1

5 Preferred embodiments of the present invention include polymers and
6 oligomers, which contain cyclohexene groups accessible to free oxygen
7 molecules. These polymers or oligomers may be prepared from any of a
8 number of methods though one preferred reaction comprises 1, 2, 3, 6,
9 tetrahydrophthalic anhydride. This anhydride is a low cost monomer derived
10 from butadiene, which makes it particularly attractive on a commercial scale.
11 The anhydride may be used to make polyester resins such as by reaction with
12 diols. It may also be reacted with hydroxy or polyhydroxy compounds to
13 produce half esters suitable for subsequent use in plastic film and materials
14 manufacture.

15

16 Example 2

17 Non-aromatic alkenyl benzyl alcohols (e.g. tetrahydrobenzyl alcohols) may
18 also be reacted with certain compounds to produce useful scavengers. For
19 instance tetrahydrobenzyl alcohol may be reacted with compounds containing
20 a carboxylic acid, acid halide, ester, anhydride and/or isocyanate functionality.
21 These compounds may be small molecules or oligomers or polymers. For
22 example, tetrahydrobenzyl alcohol may be reacted with styrene, maleic
23 anhydride copolymers or with polyfunctional isocyanates.

24

25 Example 3

26 Cyclohexene dimethanol compounds may be used to prepare oxygen
27 absorbing polyesters and polyurethanes.

28

29 Example 4

1 As another example, tetrahydrobenzoic acid and tetrahydrobenzaldehyde
2 may also be used to modify various hydroxyl functional materials.

3

4 Example 5

5 Reactions such as the functionalization of polymers may be carried out by a
6 reactive extrusion process. For instance this may be a transesterification
7 process.

8

9 Example 6

10 Cyclohexene anhydride may be used in the preparation of useful oxygen
11 scavengers. These cyclohexene anhydrides may be prepared by from a
12 diene monomer such as butadiene with maleic anhydride. Of commercial
13 attractiveness are their low cost and their ability to be converted into a
14 number of useful intermediates. In addition, they may also be used to
15 functionalize OH containing polymers. The half esters, which form rapidly
16 when a cyclic anhydride reacts with an OH group, may be subsequently
17 neutralized and the resultant materials dispersed in ionomers or ethylene
18 acrylic acid copolymers (for instance).

19

20 For ease of use, small functionalized molecules such as the reaction product
21 of four moles of tetrahydrophthalic anhydride with pentaerythritol may be
22 prepared either by heating in a mutual solvent or by a reactive extrusion
23 process. These may then be dispersed into a commodity polymer such as
24 EVA.

25

26 The cyclohexene anhydrides may also be converted into linear polyesters by
27 reaction with ethylene glycol and the like.

28

29 Example 7

1 Useful anhydrides are cyclic anhydrides and in particular the Diels Alder
2 adducts of various alkenes. Typically this will comprise 1, 3 butadiene (and
3 substituted derivatives) with other compounds able to complete a Diels Alder
4 type reaction. The resulting anhydrides may then be used in the manufacture
5 of various oxygen scavengers, and polymers containing same.

6
7 Example 8

8 Film structures, coatings, and molded articles, as well as sachets and
9 impregnated matrices, are envisaged incorporating oxygen scavengers as
10 discussed previously. Also included are transition metal catalysts such as
11 used in the prior art for catalyzing oxygen scavenging reactions. Optionally
12 initiators or triggers for the reaction may also be included.

13
14 Example 9

15
16 Preparation of a low molecular weight oxidizable oil from 3-Cyclohexene-1-
17 carbonyl chloride and triethylene glycol.

18
19 3-Cyclohexene-1-carbonyl chloride was prepared as follows:

20
21 50g of thionyl chloride was added to 27.6g of 3-cyclohexene-1-carboxylic acid
22 and the solution was stirred for two hours at 50°C. Excess thionyl chloride
23 was removed under vacuum and the resulting yellow brown oil was purified
24 by distillation under vacuum (bp 80-82°C at 18-19mm Hg).

25
26 The oil was then prepared in the following manner:

27
28 In a 250 ml flask fitted with a drying tube was placed 18.7g of 3-cyclohexene-
29 1-carbonyl chloride and 40cc of methylene chloride. A solution of 9.6g of
30 triethylene glycol in 20ml of methylene chloride was added and the reaction

-82-

1 was stirred for 2 hours at room temperature, by which time the evolution of
2 hydrochloric acid had ceased.

3

4 80ml of 10% aqueous sodium bicarbonate was added to the reaction mixture
5 and the mixture was vigorously stirred for 45 minutes. The organic layer was
6 collected, washed with water and then dried with magnesium sulphate. The
7 methylene chloride was removed under reduced pressure giving a colorless
8 oil.

9 The cyclohexene oil was compounded into a film with the following parts by
10 weight:

11

12 Oil	12
13 Silica	5
14 Benzophenone	0.3
15 Cobalt (111) acetylacetonate	0.28
16 Ethylene vinyl acetate copolymer (18% EVA)	90

17

18 A similar film was prepared using sunflower seed oil in place of the
19 cyclohexene based oil.

20

21 Both films were exposed to 4 minutes of UV light, then sealed in oxygen
22 barrier bags and stored in the dark.

23

24 Both materials scavenged oxygen after photoexposure and the sunflower oil
25 based material was a faster scavenger than the cyclohexene oil based
26 material. However, gas chromatography of the headspace of the bags post
27 oxidation revealed that there was a very large difference in the levels of
28 volatile components. The cyclohexene based material produced less than
29 3% of the volatile components produced by the sunflower oil based material.

-83-

1

2 The cyclohexene based films were stable for more than 300 days if stored at
3 room temperature in the absence of light (i.e., the oxygen concentration in a
4 sealed package containing the film specimens was essentially unchanged
5 after storage for this time period).

6

7 A similar cyclohexene based film was prepared, this time using 3,4 dimethyl-
8 3-cyclohexene-1-carbonyl chloride as the starting material. This film was a
9 much faster oxygen absorber than the film prepared from the unsubstituted
10 product. The film from the substituted produced less than 10% of the total
11 volatile components produced from an equivalent film made from sunflower
12 oil.

13

14 The dimethyl cyclohexene based films were stable for at least two hundred
15 days when stored at room temperature in the absence of light. The stability of
16 similar vegetable oil based films was limited to around 50 days.

17

18 This series of experiments revealed the following:

19

- 20 1. Cyclohexene functionalized materials are effective oxygen absorbers.
- 21 2. The speed of reaction may be increased by substituting methyl groups
22 adjacent to the double bond.
- 23 3. Cyclic alkene based materials produce much lower levels of volatile
24 oxidation products than linear alkene based materials.
- 25 4. The storage stability of cyclohexene containing films is excellent.

26

27 Example 10

28 Preparation of an oxidizable polyester resin.

29

-84-

1 In a three neck round bottom flask equipped with a Dean and Stark trap,
2 reflux condenser and nitrogen inlet/exit were placed the following materials:
3
4 cis-1,2,3,6-Tetrahydrophthalic anhydride 35.54g
5 1,4-Butanediol 20g
6
7 75ml of xylene was added, so that the trap was full of xylene and the mixture
8 was brought to reflux. The reaction was refluxed for six and a half hours:
9 0.55g of p-Toluenesulfonic acid monohydrate was added and reflux was
10 continued for a further six and a half hours.

11 25ml of xylene was removed from the trap and the mixture was refluxed for a
12 further one hour. A very viscous pale colored solution was obtained.
13

14 The solution was extracted with methanol to remove the acid catalyst, and
15 was diluted with dichloromethane prior to use.
16

17 The polymer was obtained as a 38% w/w solids solution in
18 toluene/dichloromethane. To 12.37 g of the polymer solution was taken
19 0.0213 g cobalt Ten-Cem® (OMG Inc.) in 5 mL of dichloromethane and
20 0.0069 g of Quantacure™CPTX (1-chloro-4-propoxy-thioxanthone, Great
21 Lakes Fine Chemicals) was added. The mixture was stirred for a few minutes
22 and a film was cast onto the surface of the another film at a wet thickness of
23 about 1 mm. A second film was formulated as follows and cast as above:
24 12.64 g polymer solution, 0.0318 g cobalt Ten-Cem® and 0.0074 g
25 4,4'-dimethoxybenzophenone (DMOBP, Spectrum Quality Products Inc.).
26

27 The dried films were irradiated for 2.5 minutes with a combination of
28 germicidal and backlight UV lamps. The approximate dose of UVC was
29 1350mJcm² and the approximate dose of UVA was 1950mJcm². The

-85-

- 1 irradiated films were sealed in a barrier pouch along with 120cc of air. The
2 oxygen content was monitored with time and the following results were
3 obtained:

Film #1, 4.7g, 1020 ppm Cobalt and 1470 ppm CPTX	
Elapsed Time (days)	Percent Oxygen
0	20.6
1	19.2
2	18.4
3	16.9

4

Film #2, 4.8g, 1500 ppm Cobalt and 1480 ppm DMOBP	
Elapsed Time (days)	Percent Oxygen
0	20.6
1	19.3
2	18.6
3	17.0

5

- 6 This example illustrates that polyesters derived from tetrahydrophthalic
7 anhydride are useful oxygen scavengers.

8

9 Example 11

- 10 Preparation of an oxidizable polymer from 3-Cyclohexene-1-methanol and an
11 alternating copolymer of maleic anhydride and octadecene.

12

- 13 In a three neck round bottom flask equipped with condenser and nitrogen
14 inlet was placed 20 g of poly(maleic anhydride-alt-1-octadecene). 80 cc of
15 methylene chloride was added and the mixture was stirred to dissolve. After

-86-

1 a clear solution had been obtained 3.2g of 3-Cyclohexene-1-methanol was
2 added, and washed into the flask with a further 10cc of methylene chloride.

3

4 The mixture was refluxed with stirring under nitrogen for two hours, then left
5 overnight at room temperature. The solution was refluxed for a further three
6 hours and allowed to cool to room temperature.

7

8 The polymer was obtained as a 21.9 wt. % solution in dichloromethane. To
9 20.51 g of the polymer solution was added 0.0201 g of cobalt Ten-Cem®
10 (OMG Inc., 22.5% Co by wt.) dissolved in 5 mL of toluene solution and
11 0.0038 g of Quantacure™ BMS (4-benzoyl-4'-methyl(diphenyl sulfide)
12 available from Great Lakes Fine Chemicals Ltd.). The mixture was stirred for
13 a few minutes and a film was cast using a draw down bar to a wet film
14 thickness of about 1 mm.

15

16 A second film was formulated as follows: 20.10 g polymer solution, 0.0474 g
17 cobalt Ten-Cem®, 0.0079 g 4,4'-dimethylbenzophenone (DMBP, from
18 Lancaster Synthesis). A third film was formulated as follows: 20.84 g
19 polymer solution, 0.0398 g cobalt Ten-Cem®, 0.0085 g
20 2-isopropylthioxanthone (ITX, First Chemical Co.).

21

22 The dried films were irradiated for 2.5 minutes with a combination of
23 germicidal and backlight UV lamps. The approximate dose of UVC was
24 1350 mJ/cm² and the approximate dose of UVA was 1950 mJ/cm². The
25 irradiated films were sealed in a barrier pouch along with about 120 cc of air.
26 The oxygen content was monitored with time as described elsewhere. The
27 following results were obtained:

28

-87-

Film Sample #1, 1.34g, with 1004 ppm Cobalt and 844 ppm BMS	
Elapsed Time (days)	Percent Oxygen
0	20.6
1	12.2
2	7.5
5	6.2

1

Film Sample #2, 3.04g, with 2420 ppm Cobalt and 1795 ppm DMBP	
Elapsed Time (days)	Percent Oxygen
0	20.6
1	11.8
2	10.0
5	9.7

2

3

Film Sample #3, 2.09g, with 1960 ppm Cobalt and 1860 ppm ITX	
Elapsed Time (days)	Percent Oxygen
0	20.6
1	13.8
2	10.5
5	10.0

4

5 The results suggest that the reaction of a polymeric anhydride and
6 tetrahydrobenzyl alcohol is a useful route to oxygen scavenging plastics.

7

8 Example 12

9 Preparation of a Cyclohexene containing polymer by transesterification

10

-88-

1 To a 2L resin kettle was taken 180 g of polyethylene-co-methyl acrylate
2 (EMAC® SP2260, Chevron, 24 wt. % methyl acrylate) and 1 L of toluene.
3 The kettle was equipped with a mechanical overhead stirrer, Dean-Stark trap
4 and a condenser. The kettle was heated to melt the polymer. To the stirred
5 solution was added 28.12 g of 3-cyclohexene-1-methanol, followed by the
6 addition of 2.145 g of 4-(2-hydroxyethoxy)benzophenone. (Note: this
7 benzophenone derivative was prepared by the method of Yoshino et al. *Bull.*
8 *Chem Soc. Japan*, 1973, 46, 553-6 using 4-hydroxybenzophenone, ethylene
9 carbonate and tetraethylammonium iodide.) The catalyst, titanium (IV)
10 isopropoxide (1.05g) was added. The mixture turned yellow and the reflux
11 rate increased. Heat was maintained for 4 hours and about 75 mL of
12 condensate was removed in four fractions. An additional 0.5 g of titanium
13 isopropoxide was added and heat was maintained for an additional 8 hours.
14 Additional toluene was added as needed to maintain the reaction volume.
15 Again an additional 0.5 g of catalyst was added and heat maintained for
16 another 8 hours. Analysis of the condensate showed no more production of
17 methanol. The reaction mixture was cooled to a gel and precipitated into
18 methanol. The polymer was washed with methanol until nothing was
19 extracted into the methanol fractions.
20
21 The above resin containing cyclohexene pendant groups and a covalently
22 bound benzophenone derivative was melt compounded with 500 ppm
23 vitamin E as the antioxidant and 10% of an EVA based cobalt (II) oleate
24 (Shepherd Chemicals) masterbatch. The masterbatch contained 1.0% cobalt
25 metal by weight. Samples were compression molded and cut to 197.56 cm²
26 of UVC light (254 nm) and was sealed in an oxygen barrier pouch (Cryovac
27 P640B) with 300 cc of air and was stored in the dark at room temperature.
28 Headspace oxygen levels were monitored periodically by withdrawing a 4 cc
29 sample and analyzing using a Mocon model LC 700F oxygen analyzer. The
30 following results were obtained for the 1.9 g (7.8 mil thick) sample.

1

Elapsed Time (days)	Percent Oxygen
0	20.6
1	15.6
5	5.0
14	2.1
21	1.2

2

3 This example illustrates excellent oxygen scavenging ability from this type of
4 polymer and the usefulness of a covalently bound photoinitiator.

5

6 Example 13

7 Preparation of oxidizable polyurethanes.

8

9 In a two necked 250ml flask equipped with reflux condenser and nitrogen
10 inlet/exit were placed the following materials:

11

12 1,6-Diisocyanatohexane	6.5g
13 3-Cyclohexene-1,1dimethanol	5.23g
14 2-Butanone	70ml

15

16 One drop of dibutyltin dilaurate was added and the mixture was stirred under
17 nitrogen for thirty minutes at room temperature. The mixture was then
18 brought to reflux for a further four hours and one drop of water in 10ml of
19 MEK was added. The mixture was refluxed for a further hour and then
20 allowed to cool to room temperature.

21

22 A polyurethane containing cyclic unsaturation was prepared from 1,6-
23 diisocyanatohexane and 3-cyclohexene-1,1-dimethanol. The polymer
24 (3.912 g) was taken into 10 mL dichloromethane and a solution of 0.0243 g of

-90-

1 cobalt Ten-Cem® (OMG Inc.) in 5 mL of dichloromethane was added. To the
2 stirred mixture was added 0.0084 g of 4,4'-dimethylbenzophenone (DMBP,
3 Lancaster Synthesis). The mixture was stirred for about 15 minutes. A film
4 was cast from the solution on the surface of another film at a wet thickness of
5 about 1 mm. The dried film was triggered and tested as described in
6 example 3 above.

7

3.9g, with 1400 ppm Cobalt and 2150 ppm DMBP	
Elapsed Time (days)	Percent Oxygen
0	20.6
1	18.3
4	13.1
5	9.5

8

9 These results suggest that polyurethanes derived from 3-Cyclohexene-1,1-
10 dimethanol are useful oxygen absorbers. These materials and alternative
11 formulations may be useful in formulating oxygen scavenging adhesive resins
12 for use in flexible packaging i.e., for use in lamination.

13

14 Example 14

15 Preparation of a poly (vinyl acetal) from poly(vinyl alcohol) and
16 3-Cyclohexene-1-carboxaldehyde.

17

18 In a 500ml flask equipped with nitrogen inlet/exit and mechanical stirrer was
19 placed 150 ml of a 70/30 mix of dioxane/ethanol and 10g of poly(vinylalcohol).
20 The mixture was stirred and 15.7g of 3-Cyclohexene-1-carboxaldehyde was
21 added, followed by 0.25ml conc. HCl and 5 mg of hydroquinone. The mixture
22 was refluxed for four hours, during which time the poly(vinyl alcohol) dissolved
23 and turned a pale yellow color, 0.5g of sodium acetate was added followed by

-91-

1 2.5g of urea, both in aqueous solution. The polymer precipitated and was
2 purified by addition of further dioxane then precipitation into water. The dried
3 polymer was found to contain approximately 63mole% of acetal groups.

4

5 A similar polymer was prepared from 3,4-dimethyl-3-cyclohexene-1-
6 carboxaldehyde and poly(vinyl alcohol) which contained approximately
7 65 mole% of acetal groups.

8

9 A solution of cobalt (III) acetylacetonate (20mg) and benzophenone (20mg)
10 in methylene chloride was added with stirring to a solution (1g) of each acetal
11 resin dissolved in 15ml of warm dioxane. The solution was poured into a
12 150mm diameter flat bottom petri dish and the solvent was allowed to
13 evaporate. The resultant film was held under high vacuum for 2-3 hours to
14 remove any residual solvent. A further sample containing 30% of a dibutyl
15 phthalate plasticiser was also prepared using the dimethyl substituted acetal
16 resin described above.

17

18 The film samples were exposed to 4 minutes of UVA radiation and then
19 vacuum packed in a barrier bag. 200ml of air was injected into the bag and
20 the puncture point was isolated by heat sealing. The pouch was stored in the
21 absence of light.

22

23 The following results were obtained for the unsubstituted resin:

24

Elapsed Time (days)	Percent Oxygen
0	20.6
1	no reading
3	9.9
6	7.2

-92-

12	1.2
----	-----

1

2 The following results were obtained for the disubstituted resin:

Elapsed Time (days)	Percent Oxygen
0	20.6
1	10.2
3	4.3
6	1.4
21	0

3

4 The following results were obtained from the plasticised resin:

5

Elapsed Time (days)	Percent Oxygen
0	20.6
3	3.7
4	1.8
7	0.2
12	0

6

7 These results demonstrate the following principles:

8

9 1. Cyclohexene based acetal resins are effective oxygen scavengers.

10

11 2. The substituted cyclohexene rings provide faster oxygen scavengers than
12 the unsubstituted resins.

13

14 3. A plasticiser tends to increase the rate of oxygen scavenging.

1
2
3
4 Non-limiting examples are given in Examples 15 and 16 below of
5 experimental conditions that were used for preparation of the polymers.
6 Non-limiting examples of the resin preparation followed by steam stripping as
7 well as compounding the polymers with oxidation catalyst, such as cobalt
8 oleate and a photoinitiator, such as Methanone,
9 [5'-(5'-(4-benzoylphenyl)[1,1':3', 1"-terphenyl]-4,4"-diyl]bis[phenyl- (hereinafter
10 referred to as BBP³), and extruded into a 3-layer film having a PE/oxygen
11 scavenging polymer/PE structure are provided in Examples 17 through 20
12 below.

13 Headspace studies of three layer films made by compounding catalyst
14 package with both fresh and aged (20 months stored in air at ambient
15 temperature) resins after UV triggering give a very fast rate of oxygen
16 scavenging and the resulting packages are relatively non-odorous.
17 Non-limiting examples of such studies are given in Examples 21 and 22.
18 Furthermore, the above polymer can be further diluted by a lower cost oxygen
19 permeable resin, such as EBAC or PE or EVA, down to 50 and even 25% of
20 the original concentration and still maintain a high oxygen scavenging rate, as
21 the non-limiting examples in Examples 23 and 24 show.

22
23 Example 15

24 Polymer Preparation (C1641-6)

25 550 ml of decalin® was placed in a flask. To this was added 350 g of
26 Chevron EMAC SP-2260 which has 24 weight % of methyl acrylate
27 (0.9767 moles of methyl acrylate) and 0.48 g of Irganox®1076 (0.1 mole).
28 The temperature of the mixture was gradually raised while stirring. When the

-94-

1 temperature reached approximately 120°C, 127.1 g (0.9767 moles) of
2 3-methyl-cyclohex-1-ene-4-methanol (97%) was added. When the
3 temperature reached approximately 140°C, 4.8 g of the catalyst $\text{Ti}(\text{OC}_2\text{H}_5)_4$
4 was added a portion at a time. The temperature was maintained at 170°C
5 while stirring. The course of the reaction was observed by subjecting
6 samples of the mixture to NMR at hourly intervals. The percent conversion is
7 given in Table 1 below. After 5 hours of reaction, the mixture was cooled and
8 400 ml of CHCl_3 was added and the mixture was then precipitated by adding
9 it to 4 liters of CH_3OH in a Waring blender. The precipitate is filtered and
10 washed with CH_3OH and dried in a vacuum oven at 50°C. The dried mixture
11 yielded 407.5 g of ethylene/methyl acrylate/methyl cyclohexene methyl
12 acrylate (EMCM).

13

Table 1

Time (hours)	Percent Conversion
1 hour	50%
2 hours	62.3%
3 hours	65.5%
5 hours	87.1%

14

15 390 grams of a combination of the above prepared polymer and the same
16 polymer prepared under the same conditions in a different batch, which
17 together have a conversion percentage of 68.8%, was solvent coated with
18 3.25 g cobalt-neodecanoate in 70 ml normal hexane. The mixture was
19 tumble dried for 1.5 hours and residual solvent removed in a vacuum.

20

Example 16

22

Polymer Preparation

23 600 ml of decalin was placed in a flask. To this was added 334 grams of
24 Chevron SP-2260 (0.9330 moles of methyl acrylate) and 0.44 g of Irganox®

1 1010 (0.1% mole). The temperature of the mixture was gradually raised while
2 stirring. When the temperature reached approximately 120°C, 104.6 g
3 (0.93 moles) of cyclohex-1-ene-4-methanol was added. When the
4 temperature reached approximately 140°C, 4.4 g of the catalyst $\text{Ti}(\text{OC}_2\text{H}_5)_4$
5 was added a portion at a time. The temperature was maintained at 160°C
6 while stirring. The course of the reaction was observed by subjecting
7 samples of the mixture to NMR at hourly intervals. The percent conversion is
8 given in Table 2 below. After 3 hours of reaction, the mixture was cooled and
9 400 ml of CHCl_3 was added and the mixture was then precipitated by adding
10 it to 4 liters of CH_3OH in a Waring blender. The precipitate was filtered and
11 washed with CH_3OH and dried in a vacuum oven at 50°C. The dried mixture
12 yielded 380.5 g of polymer.

13 Table 2

Time (hours)	Percent Conversion
1 hour	43.8%
2 hours	56.7%
3 hours	55.7%

14

15 185 grams of the above-prepared polymer was combined with 45 ml normal
16 hexane and 1.54 g cobalt-neodecanoate resulting in 1000 ppm of cobalt ion
17 and 0.0185 g Irganox® 1010 resulting in 100 ppm Irganox®. The mixture
18 was heated and blended and then dried in a vacuum-oven. The resulting
19 compound was extruded into a film.

20 Additionally, 185 grams of the above-prepared polymer was combined with
21 45 ml normal hexane and 1.54 g cobalt-neodecanoate (resulting in 1000 ppm
22 of cobalt ion) and 0.046 g Irganox® 1010 (resulting in 250 ppm Irganox®).
23 The mixture is heated and blended and then dried in a vacuum-oven. The
24 resulting compound is extruded into a film.

1 Example 17

2 **EMCM Made in ZSK-30 Extruder**

3 Ethylene-methyl acrylate copolymer (EMAC) was fed into a Werner &
4 Pfeiderer ZSK-30 twin screw extruder at 6 kg/hr, and the reactants and
5 catalysts were added to the extruder in a subsequent reaction zone. The
6 catalyst $\text{Ti}(\text{OC}_3\text{H}_7)_4$ was added with the reactants at 3 mol % or at a rate of
7 148 cc/hr. Irganox®/Toluene solution was added at 4.5 g/900 cc using a
8 Milton Roy 29/290 mini-pump. To obtain 100 ppm of Irganox®, it must be
9 added at 2.2 cc/min. To obtain 50 ppm of Irganox, it must be added at
10 1.1 cc/min. Cyclohexane methyl alcohol with 1,000 ppm of an antioxidant of
11 BHT was added via a Milton Roy dual head at 1958 cc/hr. Steam is injected
12 into the system at 800 cc $\text{H}_2\text{O}/\text{Hr}$ at the end of the reaction zone.

13 51 lbs of EMCM product (100 ppm Irganox® 1010, 59.3% methyl alcohol
14 (MA), 2.98 g/10 min. Melt Flow) was produced over a period of approximately
15 2 hours.

1 Example 182 EMCM Made in ZSK-30

3 45 lbs of EMCM product (100 ppm Irganox®1010, 2.38 g/10 min Melt Index)
4 was extruded over a period of approximately 3 hours. A dual steam stripping
5 setup was used in which pressurized injectors at zones 4 and 11 of the
6 extruder pumped steam at 1076 cc/hr and 728 cc/hr, respectively. Both
7 injectors were Pulse 680 pumps with a pressure of at least 800 psi, except at
8 the first measured time interval when injector (No. 4) was measured at
9 500-550 psi and injector (No. 11) was measured at 500 psi.

10 Example 1911 Co-polymerization of Styrene and 3-Cyclohexene-1-Methanol Methacrylate

12 In a 1-liter round bottom flask, 65 grams styrene (0.625 mole), 113 grams of
13 3-cyclohexene-1-methanol methacrylate (0.625 mole), 1.25 grams of Benzoyl
14 peroxide and 450 grams of toluene were mixed and degassed by freeze-thaw
15 cycles. The degassed solution was polymerized at 70-75°C for 48 hours and
16 discharged into 2 liters of methanol in a Waring Blender. The product isolated
17 was dried in a vacuum oven at 50°C for 2 hours to give 155 grams of
18 co-polymer. NMR analysis indicates it contains 48 mole % of styrene and
19 52 mole % of 3-cyclohexene-1-methanol methacrylate. Tg by DSC is 66°C.

20

21 Example 2022 Oxygen Scavenging Test of Styrene/CHMA Copolymer

23 90 weight % of the above-mentioned co-polymer and 10 weight % of a EVA
24 based Master batch containing 1 weight % of co-oleate and 1 weight % of a
25 photoinitiator (BBP³) were processed into a 8 mil thick monolayer film. A
26 100 cm² film was irradiated at both sides to receive 800 mJoules/cm² of

-98-

- 1 254 nm UV on each side and sealed into a foil bag containing 300 cc of 1%
 2 oxygen. The oxygen uptake was monitored up to 11 days at 4°C and at room
 3 temperature. The results are shown in Tables 3 (4°C) and 4 (room
 4 temperature).

5 Table 3

Time (days)	O ₂ Meas. Vol%	O ₂ Meas. Vol, ml	Vol—O ₂ Used ml	O ₂ Uptake ml/g	O ₂ Uptake Avg Rate cc/m ² /day	Instant Rate cc/m ² /day	O ₂ Capacity cc/m ² /mil
0.0	1.05	3.15	0.00	0.00	0.00	0.00	0.00
1.1	0.94	2.77	0.32	0.18	14.79	14.79	1.62
3.9	0.49	1.42	1.63	0.92	20.73	23.03	8.15
4.8	0.39	1.11	1.91	1.08	19.81	15.78	9.57
7.0	0.30	0.84	2.17	1.22	15.40	5.72	10.83
11.0	0.09	0.25	2.74	1.54	12.43	7.22	13.72

6

7

Table 4

Time (days)	O ₂ Meas. Vol%	O ₂ Meas. Vol, ml	Vol—O ₂ Used ml	O ₂ Uptake ml/g	O ₂ Uptake Avg Rate cc/m ² /day	Instant Rate cc/m ² /day	O ₂ Capacity cc/m ² /mil
0.0	1.04	3.12	0.00	0.00	0.00	0.00	0.00
1.1	0.48	1.42	1.65	1.03	75.28	75.28	8.26
3.9	0.09	0.26	2.78	1.73	35.40	19.96	13.92
4.8	0.04	0.11	2.93	1.82	30.26	7.89	14.63
7.0	0.01	0.03	3.01	1.87	21.39	1.91	15.05
11.0	0.01	0.03	3.01	1.87	13.64	0.00	15.05

8

9 Example 21

10

Polymerization of 3-cyclohexene-1-methanol acrylate

1 75 grams (0.45 mole) of 3-cyclohexene-1-methanol acrylate (CHAA), 200 ml
2 of toluene and 0.5 grams of Benzoyl peroxide were charged into a 500 ml
3 round-bottomed flask and degassed by freeze-thaw cycles. The degassed
4 solution was polymerized at 70-75°C for 48 hours. The viscous polymer
5 solution was worked up by precipitating in methanol solution in a Waring
6 blender. After vacuum drying at room temperature for 3 days, the product is a
7 rubbery clear polymer which weighs 53 grams.

8

9 Example 22

10 Headspace Analysis of O₂ Scavenging in
11 Dowlex® 3010/EMCM/Dowlex® 3010 Films

12 Oxygen scavenging analysis was performed using a Mocon HS750 with a
13 headspace volume of 300 cc. The sample tested was a 0.48 g three-layer
14 film with Dowlex® 3010 film for the two outside layers and steam stripped
15 EMCM (59% converted) for the middle layer (50 ppm Irganox® 1010). The
16 thickness of the layers was 0.5/1/0.5 +/- 0.1 Mil. The oxygen scavenging
17 portion of the middle layer comprised 1000 ppm Cobalt salt, 1000 ppm BBP³
18 and was exposed for 1.6 minutes to 254 nm UV at 1 inch to receive
19 800 mJ/cm². The oxygen scavenging was tested with 300 cc 1% O₂ at 4°C.
20 The results of the tests are given below in Table 5. These results are plotted
21 along with the results of Example 20 in Figure 2, which graphically plots %
22 oxygen in headspace against time (days). The oxygen scavenging uptake
23 capacity is based on the total weight of the three-layer film.

-100-

1

Table 5

Time (days)	O ₂ Meas. Vol%	O ₂ Meas. Vol, ml	Vol—O ₂ Used ml	O ₂ Uptake ml/g	O ₂ Uptake Avg Rate cc/m ² /day	Instant Rate cc/ m ² /day	O ₂ Capacity cc/m ² /mil
0.0	1.04	3.12	0.00	0.00	0.00	0.00	0.00
0.8	0.74	2.18	0.89	1.84	57.93	57.93	44.25
1.9	0.46	1.33	1.70	3.54	45.85	37.36	84.85
3.0	0.29	0.83	2.18	4.54	36.87	21.87	109.08
5.8	0.14	0.39	2.60	5.42	22.46	7.41	130.08
7.8	0.09	0.25	2.74	5.71	17.67	3.51	136.95

2

3 Example 23

4

Headspace Analysis of O₂ Scavenging in

5

Dowlex® 3010/EMCM/Dowlex® 3010 Films

6 Oxygen scavenging analysis was performed using a Mocon HS750 with a
7 headspace volume of 300 cc. The sample tested was a 0.47 g three-layer
8 film with Dowlex® 3010 film for the two outside layers and steam stripped
9 EMCM for the middle layer (50 ppm Irganox 1010)). The thickness of the
10 layers was 0.5/1/0.5 +/- 0.1 Mil. The oxygen scavenging portion of the middle
11 layer comprised 1000 ppm Cobalt salt, 1000 ppm BBP³ (a photoinitiator)
12 exposed for 1.6 minutes to 254 nm UV at 1 inch to receive 800 mJ/cm². The
13 oxygen scavenging was tested with 300 cc 1% O₂ at 4°C. These results are
14 plotted along with the results of Example 21 in Figure 2, which graphically
15 plots % oxygen in headspace against time (days).

1 Example 24

2 Headspace Analysis of O₂ Scavenging in Dowlex® 3010/

3 EBAC:EMCM/Dowlex® 3010 Films

4 Oxygen scavenging analysis was performed using a Mocon HS750 with a
5 headspace volume of 300 cc. The sample tested was a 0.45 g three-layer
6 film with Dowlex® 3010 film for the two outside layers and 3:1 EBAC
7 (ethylene/butyl acrylate copolymer):EMCM (ethylene/methyl acrylate/
8 cyclohexenyl methyl acrylate) for the middle layer (50 ppm Irganox® 1010)).
9 The thickness of the layers was 0.5/1/0.5 +/- 0.1 Mil. The oxygen scavenging
10 portion of the middle layer comprised 1000 ppm of Cobalt salt, 1000 ppm
11 BBP³ was exposed for 1.6 minutes to 254 nm UV at 1 inch to receive
12 800 mJ/cm². The oxygen scavenging was tested with 300 cc 1% O₂ at 4°C.
13 These results are plotted along with the results of Example 22 in Figure 3,
14 which graphically plots % oxygen in headspace against time (days).

15

16 Example 25

17 Headspace Analysis of O₂ Scavenging in Dowlex® 3010/

18 EBAC:EMCM/Dowlex® 3010 Films

19 Oxygen scavenging analysis was performed using a Mocon HS750 with a
20 headspace volume of 300 cc. The sample tested was a 0.47 g three-layer
21 film with Dowlex® 3010 film for the two outside layers and 1:1 EBAC:EMCM
22 for the middle layer (50 ppm Irganox®1010)). The thickness of the layers
23 was 0.5/1/0.5 +/- 0.1 Mil. The oxygen scavenging portion of the middle layer
24 comprised 1000 ppm Cobalt Oleate salt, 1000 ppm BBP³ exposed for
25 1.6 minutes at 254 nm UV at 1 inch to receive 800 mJ/cm². The oxygen
26 scavenging was tested with 300 cc 1% O₂ at 4°C. The results of the tests are
27 given below in Table 6. These results are plotted along with the results of
28 Example 23 in Figure 3, which graphically plots % oxygen in headspace

-102-

1 against time (days). The oxygen scavenging uptake capacity is based on the
 2 total weight of the 3-layer film.

3 Table 6

Time (days)	Head- space O ₂ (Vol%)	Head- space O ₂ (Vol, ml)	Vol—O ₂ Used (ml)	O ₂ Uptake (ml/g)	O ₂ Uptake Avg Rate (cc/m ² ·day)	Instant Rate (cc/m ² · day)	O ₂ Capacity cc/m ²
0.0	1.09	3.27	0.00	0.00	0.00	0.00	0.00
0.8	0.74	2.18	1.03	2.20	63.00	63.00	51.63
1.8	0.50	1.45	1.73	3.68	48.52	36.18	86.43
4.8	0.17	0.48	2.67	5.8	27.73	15.51	133.45
6.1	0.12	0.34	2.81	5.98	23.17	5.60	140.45
6.9	0.10	0.28	2.86	6.09	20.84	3.40	143.20
7.9	0.08	0.22	2.92	6.21	18.46	2.62	145.90

4
 5 Example 26

6 Headspace Analysis of O₂ Scavenging Capacity
 7 in Dowlex® 3010/EMCM/Dowlex® 3010 Films

8 Oxygen scavenging analysis was performed using a Mocon HS750 with a
 9 headspace volume of 300 cc. The sample tested was a 0.47 g three-layer
 10 film with Dowlex® 3010 film for the two outside layers and steam stripped
 11 EMCM for the middle layer (50 ppm Irganox®1010)). The thickness of the
 12 layers was 0.5/1/0.5 +/- 0.1 Mil. The oxygen scavenging portion of the middle
 13 layer comprised 1000 ppm Cobalt Oleate salt, 1000 ppm BBP³ exposed for
 14 1.6 minutes to 254 nm UV at 1 inch to receive 800 mJ/cm². The oxygen
 15 scavenging was tested with 300 cc air at room temperature. The O₂ uptake
 16 capacity is based on total weight of the 3-layer film. The results of the tests
 17 are given below in Table 7. These results are plotted along with the results of
 18 Example 26 in Figure 4, which graphically plots % oxygen in headspace
 19 against time (days).

Table 7

Time (days)	Head-space O ₂ (Vol%)	O ₂ Vol, (ml)	Vol-O ₂ Used (ml)	O ₂ Uptake (ml/g)	O ₂ Uptake Avg Rate (cc/m ² ·day)	Instant Rate (cc/m ² ·day)	O ₂ Capacity (cc/m ²)
0.0	20.60	61.80	0.00	0.00	0.0	0.0	0.0
1.0	13.40	39.53	21.24	43.35	1058	1058	1062
2.0	12.20	35.38	24.72	50.45	616	173	1236
3.0	11.80	33.63	25.86	52.78	437	60	1293
6.2	11.80	33.04	25.86	52.78	207	0.0	1293

1

2 Example 27

3

Headspace Analysis of O₂ Scavenging Capacity in

4

Dowlex® 3010/EBAC:EMCM/Dowlex® 3010 Films

5 Oxygen scavenging analysis was performed using a Mocon HS750 with a
6 headspace volume of 300 cc. The sample tested was a 0.45 g three-layer
7 film with Dowlex® 3010 film for the two outside layers and 2:1 EBAC:EMCM
8 for the middle layer (50 ppm Irganox 1010)). The width of the layers was
9 0.5/1/0.5 +/- 0.1 Mil. The oxygen scavenging portion of the middle layer
10 comprised 1000 ppm of Cobalt salts, 1000 ppm BBP³ exposed for
11 1.6 minutes to 254 nm UV at 1 inch to receive 800 mJ/cm². The oxygen
12 scavenging was tested with 300 cc air at room temperature. The O₂ uptake
13 capacity is based on total weight of the 3-layer film. The results of the tests
14 are given below in Table 8. These results are plotted along with the results of
15 Example 23 in Figure 4, which graphically plots % oxygen in headspace
16 against time (days).

1

Table 8

Time (days)	Head-space O ₂ (Vol%)	Head-space O ₂ Vol, (ml)	Vol-O ₂ Used (ml)	O ₂ Uptake (ml/g)	O ₂ Uptake Avg Rate (cc/m ² ·day)	Instant Rate (cc/m ² ·day)	O ₂ Capacity (cc/m ²)
0.0	20.60	61.80	0.00	0.00	0.0	0.0	0.0
1.0	17.70	52.21	8.56	18.20	426	426	428
2.0	17.40	50.46	9.43	20.05	235	43	471
3.0	17.10	48.74	10.28	21.87	174	45	514
6.2	17.10	47.88	10.28	21.87	83	0.0	514

2

3 Example 284 Taste Preference Test

5 The organoleptic quality of a film containing EMCM as the scavenging resin in
6 a multi-layer oxygen scavenging packaging structure was evaluated and
7 compared with an SBS (styrene/butadiene/styrene)-based oxygen
8 scavenging packaging structure. Films were triggered with 800 mJ/cm² of
9 254 nm UV. Packages containing ca. 200 ml of water were made and
10 vacuum/gas flushed to obtain a gas composition of 1% O₂:99% N₂. Packages
11 were stored at 40°F for seven days prior to taste testing. A forced preference
12 double blind Triangle taste test was carried out on water extracts of the
13 EMCM-based and SBS-based films.

14

15 Sensory results indicated that there was a significant difference (24 out of 28
16 respondents) between the EMCM-based and SBS-based structures. All 24
17 respondents who correctly identified the odd sample in the single test
18 preferred the taste of the water packaged in EMCM over SBS. As shown in
19 Table 9, Day 4 scavenging rates of the EMCM-based structures were lower
20 than the SBS counterpart. On Day 4, both structures had significant oxidation
21 and the obvious difference in flavor perception was attributed to the fewer and

-105-

1 less objectionable by-products (fragments after oxidation of EMCM) of the
 2 EMCM oxygen scavenging system.
 3 In a second forced preference triangle taste test, water samples in
 4 EMCM-based scavenging structures were tested against water samples
 5 packaged in a standard barrier laminate film (R660B manufactured by
 6 Cryovac Division of Sealed Air Corporation). The packaged water extract
 7 samples were submitted to a sensory panel for forced preference double blind
 8 taste testing. Samples were tested after 8 days of scavenging. A significant
 9 difference in the taste was found between the samples packaged in the
 10 EMCM and the control packages. Surprisingly, the preference was towards
 11 the EMCM structure. Open comments stated that there was no off-flavor
 12 (normally associated with the SBS-based oxygen scavenging films) in the
 13 EMCM samples and that EMCM was "pretty close in taste to the control."
 14 Headspace oxygen levels reached by the EMCM structure were ca. 0.2%
 15 (down from 1%) at Day 8. Scavenging results of the EMCM film used during
 16 this test are also listed in Table 9.

17 Table 9
 18 Oxygen Scavenging
 19 Packaging Films

Film Sample	Average Rate (cc/m ² ·day)	Average Rate (cc/m ² ·day)	Induction Period (days)	Peak Instantaneous Rate avg. (c) (cc/m ² ·day)	Peak Instantaneous Rate (cc/m ² ·day)
	Mean	St. dev.		Mean	St. dev.
SBS Film	51.0 ^a	7.8	<1	88.4 (1)	14.1
1 st Sensory test EMCM	41.6 ^a	5.3	<1	68.6 (2)	11.4
2 nd Sensory Test EMCM	30.5 ^b	5.9	<1	83.6 (2-3)	19.4

20 ^aRate at 4 days.

21 ^bRate at 8 days.

22 ^cTime to reach peak rate in days.

-107-

1 most preferred sample a score of 10. As is shown in Figure 5, the panelists
2 found the taste of the turkey packaged in control and the EMCM pouches
3 statistically equivalent. The turkey packaged in the SBS pouch was found
4 significantly less preferred than either the control or the EMCM.

5 Example 30

6 Polymerization of EMCM via high pressure autoclave reactor proceeds in a
7 steady-state continuous manner as follows. Ethylene is circulated at a rate of
8 10,000-14,000 lb/hr by a hypercompressor which compresses the ethylene to
9 16,500-22,500 psig. The compressed ethylene is injected into the autoclave
10 reactor in various positions along the reactor wall associated with the zone
11 divisions made by the reactor internals. Simultaneously, acrylate of
12 cyclohexene-1-methanol (CHAA) comonomer is injected into either the first
13 zone or the first and second zones of the reactor at a rate sufficient to
14 produce a copolymer containing from 5 to 40% CHAA, more typically
15 10%-25% by weight. The reaction is initiated by injection of a solution of
16 di-tert butyl peroxyvalate in an aliphatic solvent which also functions as a
17 chain transfer agent. The initiator is injected at a rate to provide
18 approximately 10-20 ppm (wt) of initiator in the compressed ethylene.
19 The locations of the CHAA injection are critical to the polymer being
20 produced, as is shown in U.S. Patent No. 5,571,878 which details the effects
21 of acrylate injection location on the polymerization of ethylene and an alkyl
22 acrylate comonomer in a high pressure system.

23

24 The resultant polymer exits the reactor at a rate of 1000-2000 lb/hr in a
25 multi-phase solution in ethylene to a high pressure separator. The pressure
26 of the product is reduced adiabatically through a valve to 2,000 psig pressure
27 and the unreacted ethylene and unreacted CHAA are recompressed to
28 reactor pressure and reinjected into the reactor for further polymerization.
29 Additional ethylene is added to the cycle via a primary compressor which

1 compresses the ethylene from pipeline pressure to the suction pressure of the
2 hypercompressor at a rate equal to the polymer production rate.
3 From the high pressure separator, the polymer is reduced in pressure to
4 4-10 psig for further removal of unreacted ethylene and unreacted
5 comonomer. The polymer is fed into a melt pumping device (either an
6 extruder or a gear pump) and is pelletized and transferred for packaging and
7 shipment.

8

9 Example 31

10 Synthesis of 3-Cyclohexene-1,1-Dimethanol

11 One hundred (100) parts by weight of a formaldehyde aqueous solution
12 (37 wt. % formaldehyde) was charged to a reactor. To this solution, cooled
13 externally with an ice-water bath, was added 118 parts of an aqueous sodium
14 hydroxide solution (25 wt. % sodium hydroxide) by several portions and the
15 temperature of the reaction content was maintained at 20 to 30°C. This was
16 followed by a slow addition of 54 parts of 1,2,5,6-tetrahydrobenzaldehyde at
17 such a rate that the reaction content temperature did not exceed 55°C. After
18 the exotherm dissipated, it was heated at 55°C for two hours with an external
19 heating. The product precipitated out of the solution upon cooling and was
20 collected by suction filtration. The wet-cake was washed thoroughly in the
21 funnel with copious amount of water (5 X 100 parts). The crude product was
22 allowed to dry in air overnight and purified by a recrystallization from toluene.
23 The final product was an off-white colored crystalline material (yield 70%.
24 m.p.: 92-93°C).

25

26 Example 32

27 Synthesis of 4-Cyclohexene-1,2-Dimethanol

28 A solution of one hundred (100) parts by weight of a 1,2,3,6-
29 tetrahydrophthalic anhydride in 500 parts of dry tetrahydrofuran is slowly
30 added to a stirring mixture of 28.75 parts of lithium aluminum hydride and

-109-

1 162 parts of tetrahydrofuran. After the addition is complete, the mixture is
2 refluxed for 24 hours. It is then hydrolyzed by a slow addition of a saturated
3 Rochelle salt solution until it turns white. The mixture is refluxed for an
4 additional 10 hours, allowed to room temperature, and suction filtered. The
5 solvent is removed by a distillation and the viscous liquid crude product is
6 purified by a fractional distillation under vacuum (yield 82%. b.p.: 165-170°C
7 at 12 mm).

8

9 Example 3310 Synthesis of trans-Diethyl 1,2,3,6-Tetrahydrophthalate

11 One hundred (100) parts by weight of a butadiene is dissolved into a solution
12 of 153 parts of diethyl fumarate in 650 parts of benzene at 0°C. The reaction
13 solution is then heated in a bomb at 50°C for 24 hours. The solvent is
14 removed by a distillation and the liquid crude product is purified by a fractional
15 distillation under vacuum (b.p.: 102-105°C at 2 mm).

16

17 Example 3418 Synthesis Of Polyester Containing 3-Cyclohexene-1,1-Dimethanol

19 Dimethyl terephthalate (81.9 g), ethylene glycol (43.7 g), 3-cyclohexene-
20 1,1-dimethanol (20.0 g), and titanium butoxide (0.15 g) were charged into a
21 250 mL 4-necked flask equipped with a distillation column/partial condenser.
22 The agitator and heat were turned on under nitrogen sparge (5 ml/min).
23 When the temperature reached 140-170°C, the methanol collection was
24 started. The temperature was slowly increased to 230°C. The reaction
25 temperature was held at 230-240°C until greater than 95% of the methanol
26 was collected during the course of 2-3 hours at 250-260°C under a full
27 vacuum (0.5-2 mm Hg). The final polyester was discharged into an aluminum
28 pan at about 200°C under nitrogen protection. NMR showed that the
29 polyester contained about 22 wt. % 3-cyclohexene-1,1-dimethanol unit. DSC

1 showed that the polyester was totally amorphous and had a glass transition
2 temperature of 82°C.

3

4 Example 35

5 Synthesis Of Polyester Containing 3-Cyclohexene-1,1-Dimethanol

6 Dimethyl terephthalate (1165.2 g), ethylene glycol (621.0 g), 3-cyclohexene-
7 1,1-dimethanol (284.4 g), zinc acetate dihydrate (2.08 g), and antimony oxide
8 (0.62 g) are charged into a 3-liter reaction kettle equipped with a distillation
9 column/partial condenser. The agitator and heat are turned on under
10 nitrogen sparge (10-30 ml/min). When the temperature reaches 140-170°C,
11 the methanol collection is started. After 1-3 hours at 160-190°C under
12 nitrogen, the temperature is slowly increased to 230°C. The reaction
13 temperature is held at 230-240°C until greater than 95% of the methanol is
14 collected during the course of 2-6 hours. Triphenyl phosphite (1.0 g) is then
15 added. The temperature is increased to 250-270°C, the nitrogen is stopped
16 and vacuum is applied. The reaction mixture is held for 2-4 hours at
17 250-270°C under a full vacuum (0.5-2 mm Hg). The final polyester is
18 discharged into an aluminum pan at about 200°C under nitrogen protection.

19

20 Example 36

21 Synthesis Of Polyester Containing 3-Cyclohexene-1,1-Dimethanol

22 Following the procedure described in Example 35, dimethyl terephthalate
23 (776.8 g), 1,3-propanediol (304.4 g), 3-cyclohexene-1,1-dimethanol (284.4 g),
24 and titanium butoxide (1.3 g) are charged into a 3-liter reaction kettle
25 equipped with a distillation column/partial condenser. Triphenyl phosphite
26 (0.8 g) is added before increasing the reaction temperature from 230-240°C
27 to over 250°C and applying vacuum.

1 Example 37

2 Synthesis of Polyester Containing 1,2,3,6-Tetrahydrophthalic Acid

3 Ethylene glycol (248.1 g), 1,2,3,6-tetrahydrophthalic anhydride (456.6 g),
4 hydrated monobutyltin oxide (0.7 g), and triphenyl phosphite (0.35 g) were
5 charged into a 2-liter reaction flask equipped with a distillation column/partial
6 condenser. The agitator and heat are turned on under nitrogen sparge
7 (10-30 ml/min). When the temperature reaches 160-180°C, the water
8 collection was started. After 1-3 hours at 160-190°C under nitrogen, the
9 temperature was slowly increased to 230°C. The reaction temperature was
10 held at 230-240°C until greater than 95% of the water was collected during
11 the course of 2-6 hours. The temperature was increased to 250-270°C, the
12 nitrogen was stopped and vacuum was applied. The reaction mixture was
13 held for 2-4 hours at 250-270°C under a full vacuum (0.5-2 mm Hg). The final
14 polyester was discharged into an aluminum pan at about 200°C under
15 nitrogen protection. NMR confirmed that the polyester was a
16 tetrahydrophthalic acid/ethylene glycol homopolyester. DSC showed that the
17 polyester was totally amorphous and had a glass transition temperature of
18 27°C.

19 Example 38

20 Synthesis Of Polyester Containing 3-Cyclohexene-1,1-Dimethanol
21 and 1,2,3,6-Tetrahydrophthalic Acid

1 Example 39

2 Synthesis Of Polyester Containing 3-Cyclohexene-1,1-Dimethanol
3 and 1,2,3,6-Tetrahydrophthalic Acid

4 Following the procedure described in Example 37, 2-methyl-1,3-propanediol
5 (360.4 g), 1,2,3,6-tetrahydrophthalic anhydride (913.2 g), 3-cyclohexene-
6 1,1-dimethanol (839.0 g), and hydrated monobutyltin oxide (1.0 g) are
7 charged into a 3-liter reaction kettle equipped with a distillation column/partial
8 condenser. Triphenyl phosphite (1.0 g) is added before increasing the
9 reaction temperature from 230-240°C to over 250°C and applying vacuum.

10

11 Example 40

12 Synthesis of Polyester Containing 1,2,3,6-Tetrahydrophthalic Acid

13 Following the procedure described in Example 37, 2 methyl-1,3-propanediol
14 (720.8 g), 1,2,3,6-tetrahydrophthalic anhydride (913.2 g), and hydrated
15 monobutyltin oxide (0.82 g) are charged into a 3-liter reaction kettle equipped
16 with a distillation column/partial condenser. Triphenyl phosphite (0.82 g) is
17 added before increasing the reaction temperature from 230-240°C to over
18 250°C and applying vacuum.

19

20 Example 41

21 Synthesis of Polyester Containing 1,2,3,6-Tetrahydrophthalic Acid

22 Following the procedure described in Example 37, 1,3-propanediol (608.8 g),
23 1,2,3,6-tetrahydrophthalic anhydride (913.2 g), and hydrated monobutyltin
24 oxide (0.76 g) are charged into a 3-liter reaction kettle equipped with a
25 distillation column/partial condenser. Triphenyl phosphite (0.76 g) is added
26 before increasing the reaction temperature from 230-240°C to over 250°C
27 and applying vacuum.

28

29

30

1 Example 42

2 Synthesis Of Polyester Containing 3-Cyclohexene-1,1-Dimethanol

3 Following the procedure described in Example 37, 2-methyl-1,3-propanediol
4 (180.2 g), adipic acid (584.4 g), 3-cyclohexene-1,1-dimethanol (569.6 g), and
5 hydrated monobutyltin oxide (0.67 g) are charged into a 3-liter reaction kettle
6 equipped with a distillation column/partial condenser. Triphenyl phosphite
7 (0.67 g) is added before increasing the reaction temperature from 230-240°C
8 to over 250°C and applying vacuum.

9

10 Example 43

11 Synthesis Of Polyester Containing 3-Cyclohexene-1,1-Dimethanol

12 Terephthalic acid (664.4 g), 3-cyclohexene-1,1-dimethanol (284.8 g),
13 2-methyl-1,3-propandiol (360.4 g), and hydrated monobutyltin oxide (0.75 g)
14 are charged into a 3-liter reaction kettle equipped with a distillation
15 column/partial condenser. The agitator and heat are turned on under
16 nitrogen sparge (10-30 ml/min). When the temperature reaches 200-220°C,
17 the water collection is started. After 3-7 hours at 200-230°C under nitrogen,
18 the temperature is increased to 240°C. The reaction temperature is held at
19 240°C until greater than 95% of the water is collected during the course of
20 2-6 hours. Triphenyl phosphite (0.75 g) is then added. The temperature is
21 increased to 250-270°C, the nitrogen is stopped and vacuum is applied. The
22 reaction mixture is held for 2-4 hours at 250-270°C under a full vacuum
23 (0.5-2 mm Hg). The final polyester is discharged into an aluminum pan at
24 about 200°C under nitrogen protection.

25

26 Example 44

27 Polymer prepared in Example 34 was solvent cast into a 3.5 mil film
28 containing 2 wt. % cobalt in the form of cobalt oleate and 2 wt. % of
29 anthraquinone as a long wavelength photoinitiator. A 5 x 20 cm² size film was

-114-

1 cut and irradiated under a 450 watts medium pressure mercury UV lamp for
2 2 minutes prior to sealing into a foil pouch filled with 300 cc of 1% oxygen.
3 The headspace analysis after 1 day at room temperature showed a reduction
4 in oxygen concentration to 0.91%.

5

6 Example 45

7 Polymer prepared in Example 37 was solvent cast into 2 mil film containing
8 0.2 wt.% cobalt in the form of cobalt oleate and 1 wt.% of anthraquinone.
9 Irradiated under a 450 watts medium pressure mercury UV lamp for 2 minutes
10 prior to sealing into a foil pouch filled with 300 cc of 1% oxygen. The
11 headspace analysis after 4 days at room temperature showed a reduction in
12 oxygen concentration to 0.83%.

13

14 Also included within this example and the scope of the invention are
15 compositions comprising various combinations of these substances and
16 materials.

17

18 Aspects of the present invention have been described by way of example only
19 and it should be appreciated that modifications and additions may be made
20 thereto without departing from the scope thereof.

-115-

1 WHAT IS CLAIMED:

2

3 1. A composition suitable for scavenging oxygen comprising a mixture of:

4 (a) a polymer or lower molecular weight material containing
5 substituted cyclohexene functionality according to the following
6 structure (I):

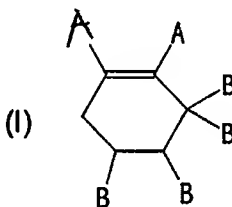
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9

10

11



12 where A may be hydrogen or methyl and either one or two of the B groups is
13 a heteroatom containing linkage which attaches the cyclohexene
14 ring to the said material. The remaining B groups are hydrogen or
15 methyl.

16

17 (b) a transition metal catalyst.

18

19 2. The composition of claim 1 where the material is blended with a carrier
20 resin.

21

22 3. The composition according to claim 2 wherein said mixture further
23 contains at least one photoinitiator.

24 4. The composition according to claim 1 wherein the heteroatom
25 containing linkage contains an ester, ether, amide, imide, urethane, or acetal
26 group.

27

28 5. An oxygen scavenger composition comprising a polymer or oligomer
29 having at least one cyclohexene group, and a transition metal salt, compound
30 or complex.

- 1 6. The composition of claim 5 further comprising a trigger enhancing
2 component which makes the scavenger susceptible to triggering from an
3 external event.
- 4 7. The composition of claim 6, wherein the trigger enhancing component is
5 selected from the group consisting of benzophenone or substituted
6 benzophenone.
- 7 8. The composition of claim 6, wherein the external event is irradiation by
8 electromagnetic radiation.
- 9 9. The composition of claim 6, wherein the external event is irradiation by
10 UV light.
- 11 10. The composition of claim 5, wherein the material is blended with a
12 carrier resin.
- 13 11. The composition of claim 5, wherein the oxygen scavenger composition
14 is in the form of a plastics resin.
- 15 12. The composition of claim 11, wherein the plastics resin comprises a
16 polyester resin.
- 17 13. The composition of claim 11, wherein the plastics resin comprises a
18 resin suitable for use in the manufacture of plastic films.
- 19 14. The composition of claim 5 wherein the composition is prepared from
20 the reaction of a tetrahydrophthalic anhydride with at least one of:
21 i) a diol;
22 ii) a hydroxy compound; or
23 iii) a polyhydroxy compound.
- 24 15. The composition of claim 14 wherein the composition is prepared by
25 heating tetrahydrophthalic anhydride with at least one of:
26 i) a diol;
27 ii) a hydroxy compound; or
28 iii) a polyhydroxy compound,
29 in a solvent.
30

-117-

- 1 16. The oxygen scavenger composition of claim 14 wherein the anhydride
2 comprises 1,2,3,6 tetrahydrophthalic anhydride, or tetrahydrophthalic
3 anhydride monomer derivable from butadiene.
- 4 17. The composition of claim 14 wherein the composition is prepared by a
5 reactive extrusion process.
- 6 18. The composition of claim 5 prepared from the reaction of a
7 tetrahydrobenzyl alcohol with one or more compounds having one or more of
8 the following functionalities:
- 9 i) carboxylic acid;
 - 10 ii) acid halide;
 - 11 iii) ester;
 - 12 iv) anhydride; and
 - 13 v) isocyanate.
- 14 19. The oxygen scavenger composition of claim 18 wherein the composition
15 is prepared by a reactive extrusion process.
- 16 20. The oxygen scavenger composition of claim 18 wherein the composition
17 is prepared from the reaction of a tetrahydrobenzyl alcohol with an ester by a
18 transesterification process.
- 19 21. The oxygen scavenger composition of claim 18 wherein the compound
20 with the anhydride functionality comprises styrene maleic anhydride
21 copolymer.
- 22 22. The oxygen scavenger composition of claim 18 wherein the compound
23 with the isocyanate functionality comprises polyfunctional isocyanate.
- 24 23. The oxygen scavenger composition of claim 5 comprising a polyester,
25 wherein the composition is prepared from cyclohexene dimethanol.
- 26 24. The oxygen scavenger composition of claim 5, wherein the composition
27 is prepared from tetrahydrobenzoic acid and a hydroxyl functional material.
- 28 25. The oxygen scavenger composition of claim 5, wherein the composition
29 is prepared from tetrahydrobenzoic acid and a hydroxyl functional material.

-118-

- 1 26. The oxygen scavenger composition of claim 5, wherein the composition
2 is prepared from tetrahydrobenzaldehyde and a hydroxyl functional material.
- 3 27. The oxygen scavenger composition of claim 5 comprising a polymer or
4 oligomer having at least one cyclohexene group, wherein some carbons of
5 the cyclohexene group form part of other ring structures within the polymer or
6 oligomer.
- 7 28. The oxygen scavenger composition of claim 5 comprising a pendant
8 cyclic alkene group, the composition prepared by a method wherein some
9 carbons of the cyclohexene group form part of the skeleton of the polymer or
10 oligomer.
- 11 29. The oxygen scavenger composition of claim 5, comprising a pendant
12 cyclohexene group, wherein the composition is prepared by a method
13 including a Diels Alder addition reaction.
- 14 30. The oxygen scavenger composition of claim 5 wherein the composition
15 is incorporated in a sachet.

-119-

1
2 31. A composition comprising a polymeric backbone, cyclic olefinic pendent
3 groups and linking groups linking the olefinic pendent groups to the polymeric
4 backbone.

5 32. A composition according to claim 31, wherein the polymeric backbone is
6 ethylenic and the linking groups are selected from the group consisting
7 of:

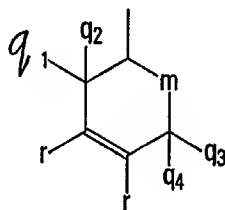
8 $-O-(CHR)_n-$; $-(C=O)-O-(CHR)_n-$; $-NH-(CHR)_n-$; $-O-(C=O)-(CHR)_n-$;

9 $-(C=O)-NH-(CHR)_n-$; and $-(C=O)-O-CHOH-CH_2-O-$;

10 wherein R is hydrogen or an alkyl group selected from the group
11 consisting of methyl, ethyl, propyl and butyl groups and where n is an
12 integer in the range from 1 to 12.

13 33. The composition of claim 31, wherein the cyclic olefinic pendent groups
14 have the structure (II):

15 (II)

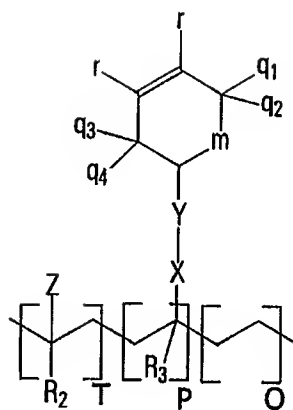


17
18 where q_1 , q_2 , q_3 , q_4 , and r are selected from the group consisting of $-H$, $-$
19 CH_3 , and $-C_2H_5$; and where m is $-(CH_2)_n-$ with n being an integer in the
20 range from 0 to 4; and wherein, when r is $-H$, at least one of q_1 , q_2 , q_3
21 and q_4 is $-H$.

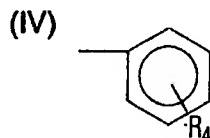
- 1 38. The composition of claim 31, wherein the polymeric backbone
2 comprises monomers selected from the group consisting of ethylene
3 and styrene.
4
- 5 38. The composition of claim 31, wherein the cyclic olefinic pendent groups
6 are grafted onto the linking groups of the polymeric backbone by an
7 esterification, transesterification, amidation or transamidation reaction.
- 8 38. The composition of claim 35, wherein the esterification,
9 transesterification, amidation or transamidation reaction is a solution
10 reaction or a reactive extrusion.
- 11 38. The composition of claim 35, wherein the esterification,
12 transesterification, amidation or transamidation reaction is catalyzed by
13 a catalyst selected from the group consisting of strong non-oxidizing
14 acids, tertiary amines, Group I alkoxides, Group IVB alkoxides, and
15 Group IVA organometallics.
- 16 38. The composition of claim 37, wherein the catalyst is selected from a
17 group consisting of toluene sulfonic acid, sodium methoxide, tetrabutyl
18 titanate, tetraisopropyl titanate, tetra-n-propyl-titanate, tetraethyl titanate,
19 2-hydroxy-pyridine and dibutyltin dilaurate.
- 20 39. The composition of claim 31, wherein the polymeric backbone, linking
21 groups and cyclic olefin pendent groups comprise repeating units, each unit
22 having a structure (III) as follows:

-121-

(III)



wherein $P+T+Q$ is 100 mol % of the total composition; P is greater than 0 mol % of the total composition; Z is selected from the group consisting of an aryl group; $-(C=O)OR_1$; $-O(C=O)R_1$; and an alkyl aryl group, structure(IV):



where R_4 is selected from the group consisting of $-CH_3$, $-C_2H_5$, and $-H$; R_1 is selected from the group consisting of $-H$, $-CH_3$, $-C_2H_5$, $-C_3H_7$ and $-C_4H_9$; R_2 and R_3 are selected from the group consisting of $-H$ and $-CH_3$; X is selected from the group consisting of $-O-$, $-NH-$, $-(C=O)O-$, $-(C=O)NH-$, $-(C=O)S-$, $-O(C=O)-$ and $-(CHR)_\ell$; ℓ is an integer in the range from 1 to 6; Y is $-(CHR)_n$, where n is an integer in the range from 0 to 12, R being selected from the group consisting of $-H$, $-CH_3$ and $-C_2H_5$; where q_1 , q_2 , q_3 , q_4 , and r are selected from the group consisting of $-H$, $-CH_3$,

-122-

1 and $-C_2H_5$; and where m is $-(CH_2)_n-$ and where n is an integer in the
2 range from 0 to 4; and wherein when r is $-H$, at least one of q_1 , q_2 , q_3
3 and q_4 is $-H$.

4 40. The composition of claim 39, wherein the cyclic olefinic pendent groups
5 are selected from the group consisting of cyclohexene-4-methylene radical,
6 1-methyl cyclohexene-4-methylene radical, 2-methyl cyclohexene-4-
7 methylene radical, 5-methyl cyclohexene-4-methylene radical, 1,2-dimethyl
8 cyclohexene-4-methylene radical, 1,5-dimethyl cyclohexene-4-methylene
9 radical, 2,5-dimethyl cyclohexene-4-methylene radical, 1,2,5-trimethyl
10 cyclohexene-4-methylene radical, cyclohexene-4-ethylene radical, 1-methyl
11 cyclohexene-4-ethylene radical, 2-methyl cyclohexene-4-ethylene radical,
12 5-methyl cyclohexene-4-ethylene radical, 1,2-dimethyl cyclohexene-4-
13 ethylene radical, 1,5-dimethyl cyclohexene-4-ethylene radical, 2,5-dimethyl
14 cyclohexene-4-ethylene radical, 1,2,5-trimethyl cyclohexene-4-ethylene
15 radical, cyclohexene-4-propylene radical, 1-methyl cyclohexene-4-propylene
16 radical, 2-methyl cyclohexene-4-propylene radical, 5-methyl cyclohexene-4-
17 propylene radical, 1,2-dimethyl cyclohexene-4-propylene radical, 1,5-dimethyl
18 cyclohexene-4-propylene radical, 2,5-dimethyl cyclohexene-4-propylene
19 radical, 1,2,5-trimethyl cyclohexene-4-propylene radical, cyclopentene-4-
20 methylene radical, 1-methyl cyclopentene-4-methylene radical, 3-methyl
21 cyclopentene-4-methylene radical, 1,2-dimethyl cyclopentene-4-methylene
22 radical, 3,5-dimethyl cyclopentene-4-methylene radical, 1,3-dimethyl
23 cyclopentene-4-methylene radical, 2,3-dimethyl cyclopentene-4-methylene
24 radical, 1,2,3-trimethyl cyclopentene-4-methylene radical, 1,2,3,5-tetramethyl
25 cyclopentene-4-methylene radical, cyclopentene-4-ethylene radical, 1-methyl
26 cyclopentene-4-ethylene radical, 3-methyl cyclopentene-4-ethylene radical,
27 1,2-dimethyl cyclopentene-4-ethylene radical, 3,5-dimethyl cyclopentene-4-
28 ethylene radical, 1,3-dimethyl cyclopentene-4-ethylene radical, 2,3-dimethyl
29 cyclopentene-4-ethylene radical, 1,2,3-trimethyl cyclopentene-4-ethylene

-123-

1 radical, 1,2,3,5-tetramethyl cyclopentene-4-ethylene radical, cyclopentene-4-
 2 propylene radical, 1-methyl cyclopentene-4-propylene radical, 3-methyl
 3 cyclopentene-4-propylene radical, 1,2-dimethyl cyclopentene-4-propylene
 4 radical, 3,5-dimethyl cyclopentene-4-propylene radical, 1,3-dimethyl
 5 cyclopentene-4-propylene radical, 2,3-dimethyl cyclopentene-4-propylene
 6 radical, 1,2,3-trimethyl cyclopentene-4-propylene radical, and 1,2,3,5-
 7 tetramethyl cyclopentene-4-propylene radical.

8 41. The composition of claim 39, wherein the composition is an
 9 ethylene/methyl acrylate/cyclohexenyl methyl acrylate terpolymer, a
 10 cyclohexenyl methyl acrylate/ethylene copolymer, a cyclohexenyl methyl
 11 methacrylate/styrene copolymer, a cyclohexenyl methyl acrylate
 12 homopolymer or a methyl acrylate/cyclohexenyl methyl acrylate copolymer.

13 42. An oxygen scavenging composition comprising a polymeric backbone,
 14 cyclic olefinic pendent groups, linking groups linking the olefinic pendent
 15 groups to the polymeric backbone and a transition metal catalyst.

16 43. A composition according to claim 42, wherein the polymeric backbone is
 17 ethylenic and the linking groups are selected from the group consisting
 18 of:

19 $-O-(CHR)_n-$; $-(C=O)-O-(CHR)_n-$; $-NH-(CHR)_n-$; $-O-(C=O)-(CHR)_n-$;

20 $-(C=O)-NH-(-CHR)_n-$; and $-(C=O)-O-CHOH-CH_2-O-$;

21 wherein R is hydrogen or an alkyl group selected from the group
 22 consisting of methyl, ethyl, propyl and butyl groups and where n is an
 23 integer in the range from 1 to 12.

24 44. The composition of claim 42, wherein the cyclic olefinic pendent groups
 25 have the structure (II):

-124-

1 (II)

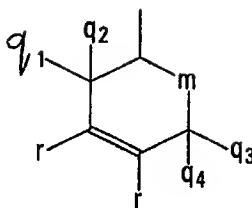
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6



7 where q_1 , q_2 , q_3 , q_4 , and r are selected from the group consisting of $-H$, $-CH_3$,
 8 and $-C_2H_5$; and where m is $-(CH_2)_n-$ with n being an integer in the range
 9 from 0 to 4; and wherein, when r is $-H$, at least one of q_1 , q_2 , q_3 and q_4 is
 10 $-H$.

11 45. The composition of claim 42, wherein the polymeric backbone
 12 comprises monomers selected from the group consisting of ethylene
 13 and styrene.

14 46. The composition of claim 42, wherein the cyclic olefinic pendent groups
 15 are grafted onto the linking groups of the polymeric backbone by a
 16 esterification, transesterification, amidation or transamidation reaction.

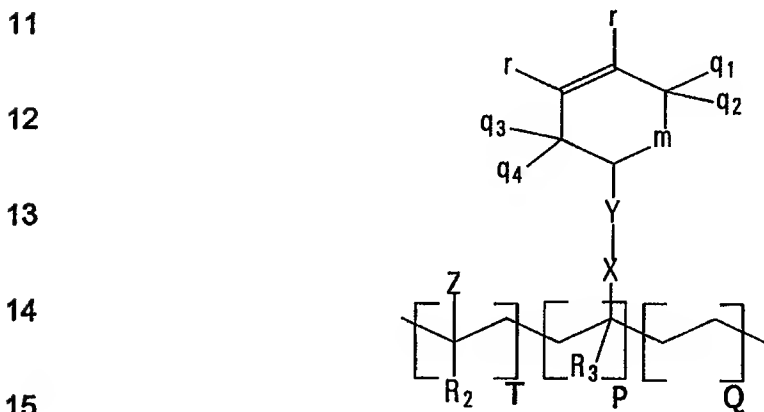
17 47. The composition of claim 46, wherein the esterification,
 18 transesterification, amidation or transamidation reaction is a solution
 19 reaction or a reactive extrusion.

20 48. The composition of claim 46, wherein the esterification,
 21 transesterification, amidation or transamidation reaction is catalyzed by
 22 a catalyst selected from the group consisting of strong non-oxidizing

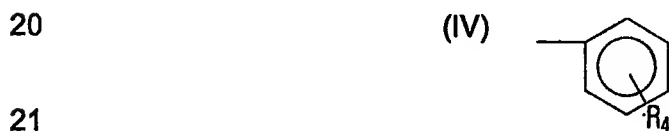
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- 1 acids, tertiary amines, Group I alkoxides, Group IVB alkoxides, and
 2 Group IVA organometallics.
- 3 49. The composition of claim 48, wherein the catalyst is selected from a
 4 group consisting of toluene sulfonic acid, sodium methoxide, tetrabutyl
 5 titanate, tetraisopropyl titanate, tetra-n-propyl-titanate, tetraethyl titanate,
 6 2-hydroxy-pyridine and dibutyltin dilaurate.
- 7 50. The composition of claim 42, wherein the polymeric backbone, linking
 8 groups and cyclic olefin pendent groups comprise repeating units, each
 9 unit having a structure (III) as follows:

10 (III)



- 16 wherein $P + T + Q$ is 100 mol % of the total composition; P is greater than 0
 17 mol % of the total composition; Z is selected from the group consisting
 18 of an aryl group; $-(C=O)OR_1$; $-O(C=O)R_1$; and an alkyl aryl group,
 19 structure (IV):



-126-

1 where R_4 is selected from the group consisting of $-\text{CH}_3$, $-\text{C}_2\text{H}_5$, and $-\text{H}$; R_1 is
 2 selected from the group consisting of $-\text{H}$, $-\text{CH}_3$, $-\text{C}_2\text{H}_5$, $-\text{C}_3\text{H}_7$ and $-\text{C}_4\text{H}_9$;
 3 R_2 and R_3 are selected from the group consisting of $-\text{H}$ and $-\text{CH}_3$; X is
 4 selected from the group consisting of $-\text{O}-$, $-\text{NH}-$, $-(\text{C}=\text{O})\text{O}-$, $-(\text{C}=\text{O})\text{NH}-$,
 5 $-(\text{C}=\text{O})\text{S}-$, $-\text{O}(\text{C}=\text{O})-$ and $-(\text{CHR})_\ell$; ℓ is an integer in the range from 1 to
 6 6; Y is $-(\text{CHR})_n$, where n is an integer in the range from 0 to 12, R being
 7 selected from the group consisting of $-\text{H}$, $-\text{CH}_3$ and $-\text{C}_2\text{H}_5$; where q_1 , q_2 ,
 8 q_3 , q_4 , and r are selected from the group consisting of $-\text{H}$, $-\text{CH}_3$, and
 9 $-\text{C}_2\text{H}_5$; and where m is $-(\text{CH}_2)_n$ and where n is an integer in the range
 10 from 0 to 4; and wherein when r is $-\text{H}$, at least one of q_1 , q_2 , q_3 and q_4 is
 11 $-\text{H}$.

12 51. The composition of claim 50, wherein the cyclic olefinic pendent groups
 13 are selected from the group consisting of cyclohexene-4-methylene
 14 radical, 1-methyl cyclohexene-4-methylene radical, 2-methyl
 15 cyclohexene-4-methylene radical, 5-methyl cyclohexene-4-methylene
 16 radical, 1,2-dimethyl cyclohexene-4-methylene radical, 1,5-dimethyl
 17 cyclohexene-4-methylene radical, 2,5-dimethyl cyclohexene-4-
 18 methylene radical, 1,2,5-trimethyl cyclohexene-4-methylene radical,
 19 cyclohexene-4-ethylene radical, 1-methyl cyclohexene-4-ethylene
 20 radical, 2-methyl cyclohexene-4-ethylene radical, 5-methyl cyclohexene-
 21 4-ethylene radical, 1,2-dimethyl cyclohexene-4-ethylene radical, 1,5-
 22 dimethyl cyclohexene-4-ethylene radical, 2,5-dimethyl cyclohexene-4-
 23 ethylene radical, 1,2,5-trimethyl cyclohexene-4-ethylene radical,
 24 cyclohexene-4-propylene radical, 1-methyl cyclohexene-4-propylene
 25 radical, 2-methyl cyclohexene-4-propylene radical, 5-methyl
 26 cyclohexene-4-propylene radical, 1,2-dimethyl cyclohexene-4-propylene
 27 radical, 1,5-dimethyl cyclohexene-4-propylene radical, 2,5-dimethyl
 28 cyclohexene-4-propylene radical, 1,2,5-trimethyl cyclohexene-4-
 29 propylene radical, cyclopentene-4-methylene radical, 1-methyl

-127-

1 cyclopentene-4-methylene radical, 3-methyl cyclopentene-4-methylene
2 radical, 1,2-dimethyl cyclopentene-4-methylene radical, 3,5-dimethyl
3 cyclopentene-4-methylene radical, 1,3-dimethyl cyclopentene-4-
4 methylene radical, 2,3-dimethyl cyclopentene-4-methylene radical, 1,2,3-
5 trimethyl cyclopentene-4-methylene radical, 1,2,3,5-tetramethyl
6 cyclopentene-4-methylene radical, cyclopentene-4-ethylene radical, 1-
7 methyl cyclopentene-4-ethylene radical, 3-methyl cyclopentene-4-
8 ethylene radical, 1,2-dimethyl cyclopentene-4-ethylene radical, 3,5-
9 dimethyl cyclopentene-4-ethylene radical, 1,3-dimethyl cyclopentene-4-
10 ethylene radical, 2,3-dimethyl cyclopentene-4-ethylene radical, 1,2,3-
11 trimethyl cyclopentene-4-ethylene radical, 1,2,3,5-tetramethyl
12 cyclopentene-4-ethylene radical, cyclopentene-4-propylene radical, 1-
13 methyl cyclopentene-4-propylene radical, 3-methyl cyclopentene-4-
14 propylene radical, 1,2-dimethyl cyclopentene-4-propylene radical, 3,5-
15 dimethyl cyclopentene-4-propylene radical, 1,3-dimethyl cyclopentene-4-
16 propylene radical, 2,3-dimethyl cyclopentene-4-propylene radical, 1,2,3-
17 trimethyl cyclopentene-4-propylene radical, and 1,2,3,5-tetramethyl
18 cyclopentene-4-propylene radical.

19 52. The composition of claim 50, wherein the composition is an
20 ethylene/methyl acrylate/cyclohexenyl methyl acrylate terpolymer, a
21 cyclohexenyl methyl acrylate/ethylene copolymer, a cyclohexenyl methyl
22 methacrylate/styrene copolymer, a cyclohexenyl methyl acrylate
23 homopolymer or a methyl acrylate/cyclohexenyl methyl acrylate copolymer.

24 53. The composition of claim 42, wherein odor and taste characteristics of
25 products packaged with material comprised of the composition are not
26 adulterated as a result of oxidation of the composition.

27 54. The composition of claim 42, wherein there is no significant
28 fragmentation of the olefinic pendent groups and linking groups from the
29 polymeric backbone as a result of oxidation of the composition.

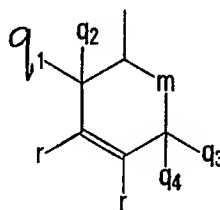
- 1 54. The composition of claim 42, wherein there is no significant
2 fragmentation of the olefinic pendent groups and linking groups from the
3 polymeric backbone as a result of oxidation of the composition.
- 4 55. The composition of claim 42, wherein the transition metal catalyst is a
5 metal salt.
- 6 56. The composition of claim 55, wherein the metal in the metal salt is
7 cobalt.
- 8 57. The composition according to claim 55, wherein the metal salt is
9 selected from the group consisting of cobalt neodecanoate, cobalt
10 2-ethylhexanoate, cobalt oleate and cobalt stearate.
- 11 58. The composition of claim 42, further comprising at least one triggering
12 material to enhance initiation of oxygen scavenging.
- 13 59. The composition of claim 58, wherein the triggering material is a photo
14 initiator.
- 15 60. An article of manufacture suitable as a container, the container inhibiting
16 oxidation of contents of the container by removing oxygen from the
17 container and by inhibiting ingress of oxygen into the container from
18 outside the container, wherein the article comprises an oxygen
19 scavenging composition which comprises a polymeric backbone, cyclic
20 olefinic pendent groups, linking groups linking the olefinic pendent
21 groups to the backbone, and a transition metal catalyst.
- 22 61. The article of manufacture of claim 60, wherein the polymeric backbone
23 is ethylenic and the linking groups are selected from the group
24 consisting of:
- 25 $-O-(CHR)_n-$; $-(C=O)-O-(CHR)_n-$; $-NH-(CHR)_n-$; $-O-(C=O)-(CHR)_n-$;
26 $-(C=O)-NH-(-CHR)_n-$; and $-(C=O)-O-CHOH-CH_2-O-$;

-129-

1 wherein R is hydrogen or an alkyl group selected from the group
 2 consisting of methyl, ethyl, propyl and butyl groups and where n is an
 3 integer in the range from 1 to 12.

4 62. The article of manufacture of claim 60, wherein the cyclic olefinic
 5 pendent groups have the structure (II):

6 (II)



10 where q_1 , q_2 , q_3 , q_4 , and r are selected from the group consisting of $-H$, $-CH_3$,
 11 and $-C_2H_5$; and where m is $-(CH_2)_n-$ and where n is an integer in the
 12 range of from 0 to 4; and wherein when r is $-H$, at least one of q_1 , q_2 , q_3
 13 and q_4 is also $-H$.

14 63. The article of manufacture of claim 60, wherein the polymeric backbone
 15 comprises monomers selected from the group consisting of ethylene and
 16 styrene.

17 64. The article of manufacture of claim 60, wherein the cyclic olefinic
 18 pendent groups are grafted onto the linking groups of the polymeric
 19 backbone by a esterification, transesterification, amidation or
 20 transamidation reaction.

21 65. The article of manufacture of claim 64, wherein the esterification,
 22 transesterification, amidation or transamidation reaction is a solution
 23 reaction or a reactive extrusion.

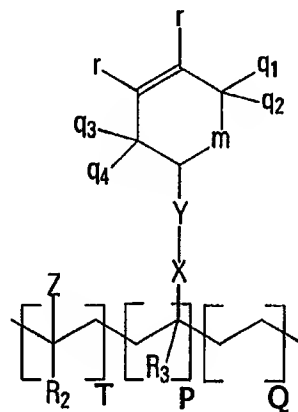
-130-

1 66. The article of manufacture of claim 64, wherein the esterification,
 2 transesterification, amidation or transamidation reaction is catalyzed by
 3 a catalyst selected from the group consisting of strong non-oxidizing
 4 acids, tertiary amines, Group I alkoxides, Group IVB alkoxides, and
 5 Group IVA organometallics.

6 67. The article of manufacture of claim 66, wherein the catalyst is selected
 7 from the group consisting of toluene sulfonic acid, sodium methoxide,
 8 tetrabutyl titanate, tetraisopropyl titanate, tetra-n-propyl-titanate,
 9 tetraethyl titanate, 2-hydroxy-pyridine and dibutyltin dilaurate.

10 68. The article of manufacture of claim 60, wherein the backbone, linking
 11 groups and cyclic olefin pendent groups comprise repeating units, each
 12 unit having a structure (III) as follows:

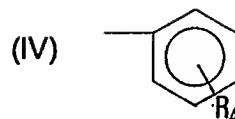
(III)



18
 19 wherein P+T + Q is 100 mol % of the total composition; P is greater than 0
 20 mol % of the total composition; Z is selected from the group consisting
 21 of an aryl group, $-(C=O)OR_1$, $-O(C=O)R_1$ and an alkyl aryl group,
 22 structure (IV):

23

-131-



where R_4 is selected from the group consisting of $-\text{CH}_3$, $-\text{C}_2\text{H}_5$, and $-\text{H}$; R_1 is selected from the group consisting of $-\text{H}$, $-\text{CH}_3$, $-\text{C}_2\text{H}_5$, $-\text{C}_3\text{H}_7$ and $-\text{C}_4\text{H}_9$; R_2 and R_3 are selected from the group consisting of $-\text{H}$ and CH_3 ; X is selected from the group consisting of $\text{O}-$, $-\text{NH}-$, $-(\text{C}=\text{O})\text{O}-$, $-(\text{C}=\text{O})\text{NH}-$, $-(\text{C}=\text{O})\text{S}-$, $-\text{O}(\text{C}=\text{O})-$ and $-(\text{CHR})_\ell-$; ℓ is an integer selected from the group consisting of 1, 2, 3, 4, 5 and 6; Y is $-(\text{CHR})_n-$, where n is an integer in the range from 0 to 12 and R is selected from the group consisting of $-\text{H}$, $-\text{CH}_3$ and C_2H_5 ; and where q_1 , q_2 , q_3 , q_4 , and r are selected from the group consisting of $-\text{H}$, $-\text{CH}_3$, and $-\text{C}_2\text{H}_5$; and where m is $-(\text{CH}_2)_n-$ and where n is an integer in the range of from 0 to 4; and wherein when r is $-\text{H}$, at least one of q_1 , q_2 , q_3 , and q_4 is $-\text{H}$.

69. The article of manufacture of claim 60, wherein the cyclic olefinic pendent groups are selected from the group consisting of cyclohexene-4-methylene radical, 1-methyl cyclohexene-4-methylene radical, 2-methyl cyclohexene-4-methylene radical, 5-methyl cyclohexene-4-methylene radical, 1,2-dimethyl cyclohexene-4-methylene radical, 1,5-dimethyl cyclohexene-4-methylene radical, 2,5-dimethyl cyclohexene-4-methylene radical, 1,2,5-trimethyl cyclohexene-4-methylene radical, cyclohexene-4-ethylene radical, 1-methyl cyclohexene-4-ethylene radical, 2-methyl cyclohexene-4-ethylene radical, 5-methyl cyclohexene-4-ethylene radical, 1,2-dimethyl cyclohexene-4-ethylene radical, 1,5-dimethyl cyclohexene-4-ethylene radical, 2,5-dimethyl cyclohexene-4-ethylene radical, 1,2,5-trimethyl cyclohexene-4-ethylene

-132-

1 radical, cyclohexene-4-propylene radical, 1-methyl cyclohexene-4-propylene
2 radical, 2-methyl cyclohexene-4-propylene radical, 5-methyl cyclohexene-4-
3 propylene radical, 1,2-dimethyl cyclohexene-4-propylene radical, 1,5-dimethyl
4 cyclohexene-4-propylene radical, 2,5-dimethyl cyclohexene-4-propylene
5 radical, 1,2,5-trimethyl cyclohexene-4-propylene radical, cyclopentene-4-
6 methylene radical, 1-methyl cyclopentene-4-methylene radical, 3-methyl
7 cyclopentene-4-methylene radical, 1,2-dimethyl cyclopentene-4-methylene
8 radical, 3,5-dimethyl cyclopentene-4-methylene radical, 1,3-dimethyl
9 cyclopentene-4-methylene radical, 2,3-dimethyl cyclopentene-4-methylene
10 radical, 1,2,3-trimethyl cyclopentene-4-methylene radical, 1,2,3,5-tetramethyl
11 cyclopentene-4-methylene radical, cyclopentene-4-ethylene radical, 1-methyl
12 cyclopentene-4-ethylene radical, 3-methyl cyclopentene-4-ethylene radical,
13 1,2-dimethyl cyclopentene-4-ethylene radical, 3,5-dimethyl cyclopentene-4-
14 ethylene radical, 1,3-dimethyl cyclopentene-4-ethylene radical, 2,3-dimethyl
15 cyclopentene-4-ethylene radical, 1,2,3-trimethyl cyclopentene-4-ethylene
16 radical, 1,2,3,5-tetramethyl cyclopentene-4-ethylene radical, cyclopentene-4-
17 propylene radical, 1-methyl cyclopentene-4-propylene radical, 3-methyl
18 cyclopentene-4-propylene radical, 1,2-dimethyl cyclopentene-4-propylene
19 radical, 3,5-dimethyl cyclopentene-4-propylene radical, 1,3-dimethyl
20 cyclopentene-4-propylene radical, 2,3-dimethyl cyclopentene-4-propylene
21 radical, 1,2,3-trimethyl cyclopentene-4-propylene radical, and 1,2,3,5-
22 tetramethyl cyclopentene-4-propylene radical.

23 70. The article of manufacture of claim 60, wherein the composition is an
24 ethylene/methyl acrylate/cyclohexenyl methyl acrylate terpolymer, a
25 cyclohexenyl methyl acrylate/ethylene copolymer, a cyclohexenyl methyl
26 methacrylate/styrene copolymer, a cyclohexenyl methyl acrylate
27 homopolymer or a methyl acrylate/cyclohexenyl methyl acrylate copolymer.
28

-133-

- 1 71. The article of manufacture according to claim 60, wherein the transition
2 metal catalyst is a metal salt.
3
4
- 5 72. The article of manufacture according to claim 71, wherein the metal in
6 the metal salt is cobalt.
7
- 8 73. The article of manufacture of according to claim 71, wherein the metal
9 salt is selected from the group consisting of cobalt neodecanoate, cobalt
10 2-ethylhexanoate, cobalt oleate and cobalt stearate.
11
12
- 13 74. The article of manufacture of claim 60, further comprising at least one
14 triggering material to enhance initiation of oxygen scavenging.
15
- 16 75. The article of manufacture of claim 74, wherein the triggering material is
17 a photoinitiator.
18
19
- 20 76. The article of manufacture of claim 60, wherein odor and taste
21 characteristics of products packaged with material comprised of the
22 composition are not adulterated as a result of oxidation of the composition.
23
- 24 77. The article of manufacture of claim 60, wherein there is no significant
25 fragmentation of the olefinic pendent groups and linking groups from the
26 polymeric backbone as a result of oxidation of the composition.
27
- 28 78. The article of manufacture of claim 60 wherein the article is a
29 package.
30

- 1 79. The article of manufacture of claim 78, wherein the package
2 comprises a flexible film having a thickness of at most 10 mil or a flexible
3 sheet having a thickness of at least 10 mil.
4
- 5 80. The article of manufacture of claim 78, wherein the oxygen
6 scavenging system of the package comprises at least one additional layer
7 selected from among oxygen barrier layers, polymeric selective layers, and
8 heat seal layers.
9
- 10 81. The article of manufacture of claim 78, wherein the article is a
11 package with a food product located within the package.
- 12 82. The article of manufacture of claim 78, wherein the article is a
13 package for packaging a cosmetic, chemical, electronic device, pesticide or a
14 pharmaceutical composition.
15
- 16 83. A multi-layer film comprising the article of manufacture according to
17 claim 60, and at least one additional functional layer.
18
- 19 84. The multi-layer film according to claim 83, wherein at least one
20 additional layer is selected from among oxygen barrier layers, polymeric
21 selective barrier layers, structural layers and heat seal layers.
22
- 23 85. The multi-layer film according to claim 83, wherein the at least one
24 additional layer is an oxygen barrier layer.
25
- 26 86. The multi-layer film according to claim 85, further comprising at least
27 one polymeric selective barrier layer.
28
- 29 87. The multi-layer film according to claim 85, further comprising at least
30 one heat seal layer.

- 1
- 2 88. The multi-layer film according to claim 85, further comprising at least
- 3 one structural layer.
- 4
- 5 89. The article of claim 60, wherein the article is a rigid container, sealing
- 6 gasket, patch, container closure device, bottle cap, bottle cap insert or
- 7 molded or thermoformed shape.
- 8
- 9 90. The article of claim 89, wherein the molded or thermoformed shape is
- 10 a bottle or tray.
- 11
- 12 91. A layer suitable for scavenging oxygen comprising:
- 13 i) a polymer backbone;
- 14 ii) cyclic olefinic pendent groups;
- 15 iii) linking groups linking the backbone with the pendent groups; and
- 16 iv) a transition metal catalyst.
- 17
- 18 92. The layer of claim 91, wherein odor and taste characteristics of
- 19 products packaged with material comprised of the layer are not adulterated as
- 20 a result of oxidation of the layer.
- 21
- 22 93. The layer of claim 91, wherein there is no significant fragmentation of
- 23 the olefinic pendent groups and linking groups from the polymeric backbone
- 24 as a result of oxidation of the layer.
- 25
- 26 94. A layer according to claim 91, wherein the transition metal catalyst is
- 27 a metal salt.
- 28
- 29 95. A layer according to claim 94, wherein the transition metal in the
- 30 metal salt is cobalt.

1

2 96. A layer according to claim 94, wherein the metal salt selected from
3 the group consisting of cobalt neodecanoate, cobalt 2-ethylhexanoate, cobalt
4 oleate and cobalt stearate.

5

6 97. A layer according to claim 91, wherein said layer in addition
7 comprises polymeric diluent.

8

9 98. A layer according to claim 97, wherein said diluent is a thermoplastic
10 polymer.

11 99. A layer according to claim 91, wherein said layer is adjacent to one or
12 more additional layers.

13

14 100. A layer according to claim 99, wherein at least one additional layer is
15 an oxygen barrier.

16

17 101. A layer according to claim 100, wherein said oxygen barrier
18 comprises a member of the group consisting of poly(ethylene-vinyl alcohol),
19 polyacrylonitrile, poly(vinyl chloride), polyamides, poly(vinylidene dichloride),
20 poly(ethylene terephthalate), silica, metal foil and metalized polymeric films.

21

22 102. A layer according to claim 99, wherein one or more of said additional
23 layer or layers is coextruded with said layer.

24

25 103. A layer according to claim 99, wherein one or more of said additional
26 layer or layers is laminated onto said layer.

27

28 104. A layer according to claim 99, wherein one or more of said additional
29 layer or layers is coated onto said layer.

30

-137-

- 1 105. A layer according to claim 99, wherein said layer is flexible.
2
- 3 106. A layer according to claim 99, wherein said layer is transparent.
4
- 5 107. An article for packaging wherein the article comprises a layer
6 according to claim 91.
7
- 8 108. A process of making a polymer material by a process selected from
9 the group consisting of esterification, transesterification, amidation,
10 transamidation and direct polymerization, wherein the polymer material
11 comprises a polymer backbone, cyclic olefinic pendent groups, linking groups
12 linking the backbone with the pendent groups.
- 13 109. The process of claim 108, wherein making the polymer material
14 comprises the steps of:
- 15 a) selecting polymers from the group consisting of styrene/maleic
16 anhydride, ethylene/maleic anhydride, ethylene/acrylic acid,
17 ethylene/methacrylic acid, acrylic acid, methacrylic acid, styrene/methacrylic
18 acid, ethylene/methyl acrylate, ethylene/ethyl acrylate, ethylene/butyl acrylate,
19 methyl methacrylate, methyl acrylate, and styrene/methyl methacrylate to
20 form a mixture and combining the polymers with a esterifying/transesterifying
21 compound selected from the group consisting of cyclohexene-4-methanol,
22 1-methyl cyclohexene-4-methanol, 2-methyl cyclohexene-4-methanol,
23 5-methyl cyclohexene-4-methanol, 1,2-dimethyl cyclohexene-4-methanol,
24 1,5-dimethyl cyclohexene-4-methanol, 2,5-dimethyl cyclohexene-4-methanol,
25 1,2,5-trimethyl cyclohexene-4-methanol, cyclohexene-4-ethanol, 1-methyl
26 cyclohexene-4-ethanol, 2-methyl cyclohexene-4-ethanol, 5-methyl
27 cyclohexene-4-ethanol, 1,2-dimethyl cyclohexene-4-ethanol, 1,5-dimethyl
28 cyclohexene-4-ethanol, 2,5-dimethyl cyclohexene-4-ethanol, 1,2,5-trimethyl

-138-

- 1 cyclohexene-4-ethanol, cyclohexene-4-propanol, 1-methyl cyclohexene-4-
2 propanol, 2-methyl cyclohexene-4-propanol, 5-methyl cyclohexene-4-
3 propanol, 1,2-dimethyl cyclohexene-4-propanol, 1,5-dimethyl cyclohexene-4-
4 propanol, 2,5-dimethyl cyclohexene-4-propanol, 1,2,5-trimethyl cyclohexene-
5 4-propanol, cyclopentene-4-methanol, 1-methyl cyclopentene-4-methanol, 3-
6 methyl cyclopentene-4-methanol, 1,2-dimethyl cyclopentene-4-methanol, 3,5-
7 dimethyl cyclopentene-4-methanol, 1,3-dimethyl cyclopentene-4-methanol,
8 2,3-dimethyl cyclopentene-4-methanol, 1,2,3-trimethyl cyclopentene-4-
9 methanol, 1,2,3,5-tetramethyl cyclopentene-4-methanol, cyclopentene-4-
10 ethanol, 1-methyl cyclopentene-4-ethanol, 3-methyl cyclopentene-4-ethanol,
11 1,2-dimethyl cyclopentene-4-ethanol, 3,5-dimethyl cyclopentene-4-ethanol,
12 1,3-dimethyl cyclopentene-4-ethanol, 2,3-dimethyl cyclopentene-4-ethanol,
13 1,2,3-trimethyl cyclopentene-4-ethanol, 1,2,3,5-tetramethyl cyclopentene-4-
14 ethanol, cyclopentene-4-propanol, 1-methyl cyclopentene-4-propanol, 3-
15 methyl cyclopentene-4-propanol, 1,2-dimethyl cyclopentene-4-propanol, 3,5-
16 dimethyl cyclopentene-4-propanol, 1,3-dimethyl cyclopentene-4-propanol,
17 2,3-dimethyl cyclopentene-4-propanol, 1,2,3-trimethyl cyclopentene-4-
18 propanol, and 1,2,3,5-tetramethyl cyclopentene-4-propanol;
- 19 b) heating the polymers and esterifying/transesterifying compounds
20 selected in (a) to form a polymer melt;
- 21 c) processing the melt in an extruder under esterification/transesterification
22 conditions with esterification/transesterification catalysts and antioxidants
23 protecting the melt from oxidation during extrusion, so that the polymer melt
24 undergoes esterification of polymeric anhydrides with cyclic olefin pendent
25 groups, esterification of polymeric acids with cyclic olefin pendent groups or
26 exchange of alkyl groups of polymeric esters with cyclic olefin pendent
27 groups; and
- 28 d) removing volatile organic products and by-products from the melt.

-139-

- 1 110. The process of claim 108, wherein making the polymer material
2 comprises the steps of:
- 3 a) selecting polymers from the group consisting of styrene/maleic
4 anhydride, ethylene/maleic anhydride, ethylene/acrylic acid,
5 ethylene/methacrylic acid, acrylic acid, methacrylic acid, styrene/methacrylic
6 acid, ethylene/methyl acrylate, ethylene/ethyl acrylate, ethylene/butyl acrylate,
7 methyl methacrylate, methyl acrylate, and styrene/methyl methacrylate to
8 form a mixture and combining the polymers with a amidizing/transamidizing
9 compound selected from the group consisting of cyclohexene-4-methyl
10 amine, 1-methyl cyclohexene-4-methyl amine, 2-methyl cyclohexene-4-methyl
11 amine, 5-methyl cyclohexene-4-methyl amine, 1,2-dimethyl cyclohexene-4-
12 methyl amine, 1,5-dimethyl cyclohexene-4-methyl amine, 2,5-dimethyl
13 cyclohexene-4-methyl amine, 1,2,5-trimethyl cyclohexene-4-methyl amine,
14 cyclohexene-4-ethyl amine, 1-methyl cyclohexene-4-ethyl amine, 2-methyl
15 cyclohexene-4-ethyl amine, 5-methyl cyclohexene-4-ethyl amine, 1,2-dimethyl
16 cyclohexene-4-ethyl amine, 1,5-dimethyl cyclohexene-4-ethyl amine, 2,5-
17 dimethyl cyclohexene-4-ethyl amine, 1,2,5-trimethyl cyclohexene-4-ethyl
18 amine, cyclohexene-4-propyl amine, 1-methyl cyclohexene-4-propyl amine, 2-
19 methyl cyclohexene-4-propyl amine, 5-methyl cyclohexene-4-propyl amine,
20 1,2-dimethyl cyclohexene-4-propyl amine, 1,5-dimethyl cyclohexene-4-propyl
21 amine, 2,5-dimethyl cyclohexene-4-propyl amine, 1,2,5-trimethyl
22 cyclohexene-4-propyl amine, cyclopentene-4-methyl amine, 1-methyl
23 cyclopentene-4-methyl amine, 3-methyl cyclopentene-4-methyl amine, 1,2-
24 dimethyl cyclopentene-4-methyl amine, 3,5-dimethyl cyclopentene-4-methyl
25 amine, 1,3-dimethyl cyclopentene-4-methyl amine, 2,3-dimethyl
26 cyclopentene-4-methyl amine, 1,2,3-trimethyl cyclopentene-4-methyl amine,
27 1,2,3,5-tetramethyl cyclopentene-4-methyl amine, cyclopentene-4-ethyl
28 amine, 1-methyl cyclopentene-4-ethyl amine, 3-methyl cyclopentene-4-ethyl
29 amine, 1,2-dimethyl cyclopentene-4-ethyl amine, 3,5-dimethyl cyclopentene-

-140-

- 1 4-ethyl amine, 1,3-dimethyl cyclopentene-4-ethyl amine, 2,3-dimethyl
2 cyclopentene-4-ethyl amine, 1,2,3-trimethyl cyclopentene-4-ethyl amine,
3 1,2,3,5-tetramethyl cyclopentene-4-ethyl amine, cyclopentene-4-propyl
4 amine, 1-methyl cyclopentene-4-propyl amine, 3-methyl cyclopentene-4-
5 propyl amine, 1,2-dimethyl cyclopentene-4-propyl amine, 3,5-dimethyl
6 cyclopentene-4-propyl amine, 1,3-dimethyl cyclopentene-4-propyl amine, 2,3-
7 dimethyl cyclopentene-4-propyl amine, 1,2,3-trimethyl cyclopentene-4-propyl
8 amine, and 1,2,3,5-tetramethyl cyclopentene-4-propyl amine;
- 9 b) heating the polymers and amidizing/transamidizing compounds selected
10 in (a) to form a polymer melt;
- 11 c) processing the melt in an extruder under amidation/transamidation
12 conditions with amidation/transamidation catalysts and antioxidants protecting
13 the melt from oxidation during extrusion, so that the polymer melt undergoes
14 amidation of polymeric anhydrides with cyclic olefin pendent groups,
15 amidation of polymeric acids with cyclic olefin pendent groups or exchange of
16 alkyl groups of polymeric esters with cyclic olefin pendent groups; and
- 17 d) removing volatile organic products and by-products from the melt.
- 18 111. The process of claim 108, wherein the making of the polymer material
19 comprises the steps of:
- 20 (a) adding to an autoclave, ethylene and a vinyl monomer comprising
21 a pendent cyclohexene;
- 22 (b) stirring the ethylene and the vinyl monomer in the autoclave to
23 achieve a mixture;
- 24 (c) adding a polymerization initiator before, during or after the stirring
25 step;
- 26 (d) polymerizing the mixture to achieve a polymer; and
27 (e) isolating and purifying the polymer.

-141-

1
2 112. The process of claim 111, wherein in step (a) an alpha-olefin is added to
3 the autoclave along with the ethylene and the vinyl monomer and in
4 step (b) the alpha-olefin is stirred with the ethylene and the vinyl
5 monomer to achieve the mixture.
6

7 113. The process of claim 109, wherein the polymeric backbone is ethylenic
8 and the linking groups are selected from the group consisting of:

9 $-\text{O}-(\text{CHR})_n-; -(\text{C}=\text{O})-\text{O}-(\text{CHR})_n-; -\text{NH}-(\text{CHR})_n-;$

10 $-\text{O}-(\text{C}=\text{O})-(\text{CHR})_n-; -(\text{C}=\text{O})-\text{NH}-(\text{CHR})_n-;$ and

11 $-(\text{C}=\text{O})-\text{O}-\text{CHOH}-\text{CH}_2-\text{O}-;$

12 where R is hydrogen or an alkyl group selected from the group
13 consisting of methyl, ethyl, propyl and butyl groups and where n is an
14 integer in the range from 1 to 12.

15 114. The process of claim 110, wherein the polymeric backbone is ethylenic
16 backbone and the linking group is:

17 $-(\text{C}=\text{O})-\text{NH}-(\text{CHR})_n$

18 where R is hydrogen or an alkyl group selected from the group
19 consisting of methyl, ethyl, propyl and butyl groups and where n is an
20 integer in the range from 1 to 12.

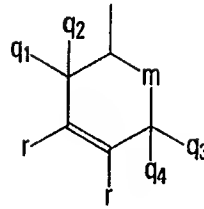
21 115. The process of claim 108, wherein the material is an oxygen scavenging
22 composition further comprising a transition metal catalyst.

-142-

- 1 116. The process of claim 115, wherein the transition metal catalyst is a
2 metal salt.
3
- 4 117. The process of claim 116, wherein the metal in the metal salt is cobalt.
5
- 6 118. The process according to claim 116, wherein the metal salt is selected
7 from the group consisting of cobalt neodecanoate, cobalt 2-ethylhexanoate,
8 cobalt oleate and cobalt stearate.
9
10
- 11 119. The process of claim 115, wherein the oxygen scavenging composition
12 further comprises at least one triggering material to enhance initiation of
13 oxygen scavenging.
14
- 15 120. The process of claim 119, wherein the triggering material is a
16 photoinitiator.
17
18
- 19 121. The process of claim 108, wherein the cyclic olefinic pendent groups
20 have the structure (II):

-143-

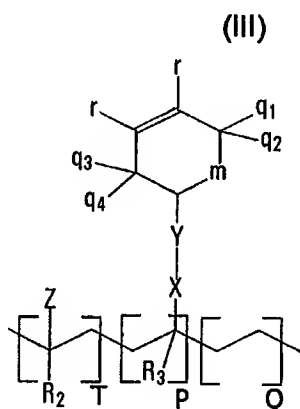
(II)



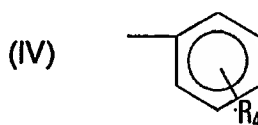
- where q_1 , q_2 , q_3 , q_4 , and r are selected from the group consisting of $-H$, $-CH_3$, and $-C_2H_5$; and where m is $-(CH_2)_n-$ and where n is an integer in the range of from 0 to 4; and wherein when r is $-H$, at least one of q_1 , q_2 , q_3 and q_4 is $-H$.
122. The process of claim 108, wherein the functional groups with attached cyclic olefinic pendent groups are grafted onto the linking backbone by a esterification, transesterification, amidation or transamidation reaction.
123. The process of claim 108, wherein the reaction is a solution reaction or a reactive extrusion.
124. The process of claim 108, wherein the esterification, transesterification, amidation or transamidation reaction is catalyzed by a catalyst selected from the group consisting of strong non-oxidizing acids, tertiary amines, Group I alkoxides, Group IVB alkoxides, Group IVA organometallics.
125. The process of claim 124, wherein the catalyst is selected from the group consisting of toluene sulfonic acid, sodium methoxide, tetrabutyl titanate, tetraisopropyl titanate, tetra-*n*-propyl-titanate, tetraethyl titanate, 2-hydroxy-pyridine and dibutyltin dilaurate.

-144-

126. The process of claim 108, wherein the backbone, linking groups and cyclic olefin pendent groups comprise repeating units, each unit having a structure (III) as follows:



wherein $P + T + Q$ is 100 mol % of the total composition; P is greater than 0;
 Z is selected from the group consisting of an aryl group, $-(C=O)OR_1$,
 $-O(C=O)R_1$ and an alkyl aryl group, structure (IV):



where R_4 is selected from the group consisting of $-H$, $-CH_3$ and $-C_2H_5$; R_1 is
 selected from the group consisting of $-H$, $-CH_3$, $-C_2H_5$, $-C_3H_5$ and $-C_4H_7$;
 R_2 and R_3 is selected from the group consisting of $-H$ and CH_3 ; X is
 selected from the group consisting of $O-$, $-NH-$, $-(C=O)O-$, $-(C=O)NH-$,
 $-(C=O)S-$, $-O(C=O)-$ and $-(CHR)_\ell$; ℓ is an integer selected from the
 group consisting of 1, 2, 3, 4, 5 and 6; Y is $-(CHR)_n$, where n is an
 integer in the range from 0 to 12 where R is selected from the group

-145-

1 consisting of $-H$, $-CH_3$ and $-C_2H_5$; where q_1 , q_2 , q_3 , q_4 , and r are selected
2 from the group consisting of $-H$, $-CH_3$, and $-C_2H_5$; and where m is
3 $-(CH_2)_n-$ and where n is an integer in the range of from 0 to 4; and
4 wherein when r is $-H$, at least one of q_1 , q_2 , q_3 and q_4 is $-H$.

5 127. The process of claim 108, wherein the cyclic olefinic pendent groups are
6 selected from the group consisting of cyclohexene-4-methylene radical,
7 1-methyl cyclohexene-4-methylene radical, 2-methyl cyclohexene-4-
8 methylene radical, 5-methyl cyclohexene-4-methylene radical,
9 1,2-dimethyl cyclohexene-4-methylene radical, 1,5-dimethyl
10 cyclohexene-4-methylene radical, 2,5-dimethyl cyclohexene-4-
11 methylene radical, 1,2,5-trimethyl cyclohexene-4-methylene radical,
12 cyclohexene-4-ethylene radical, 1-methyl cyclohexene-4-ethylene
13 radical, 2-methyl cyclohexene-4-ethylene radical, 5-methyl
14 cyclohexene-4-ethylene radical, 1,2-dimethyl cyclohexene-4-ethylene
15 radical, 1,5-dimethyl cyclohexene-4-ethylene radical, 2,5-dimethyl
16 cyclohexene-4-ethylene radical, 1,2,5-trimethyl cyclohexene-4-ethylene
17 radical, cyclohexene-4-propylene radical, 1-methyl cyclohexene-4-
18 propylene radical, 2-methyl cyclohexene-4-propylene radical, 5-methyl
19 cyclohexene-4-propylene radical, 1,2-dimethyl cyclohexene-4-propylene
20 radical, 1,5-dimethyl cyclohexene-4-propylene radical, 2,5-dimethyl
21 cyclohexene-4-propylene radical, 1,2,5-trimethyl cyclohexene-4-
22 propylene radical, cyclopentene-4-methylene radical, 1-methyl
23 cyclopentene-4-methylene radical, 3-methyl cyclopentene-4-methylene
24 radical, 1,2-dimethyl cyclopentene-4-methylene radical, 3,5-dimethyl
25 cyclopentene-4-methylene radical, 1,3-dimethyl cyclopentene-4-
26 methylene radical, 2,3-dimethyl cyclopentene-4-methylene radical,
27 1,2,3-trimethyl cyclopentene-4-methylene radical, 1,2,3,5-tetramethyl
28 cyclopentene-4-methylene radical, cyclopentene-4-ethylene radical,
29 1-methyl cyclopentene-4-ethylene radical, 3-methyl cyclopentene-4-

-146-

1 ethylene radical, 1,2-dimethyl cyclopentene-4-ethylene radical,
2 3,5-dimethyl cyclopentene-4-ethylene radical, 1,3-dimethyl
3 cyclopentene-4-ethylene radical, 2,3-dimethyl cyclopentene-4-ethylene
4 radical, 1,2,3-trimethyl cyclopentene-4-ethylene radical,
5 1,2,3,5-tetramethyl cyclopentene-4-ethylene radical, cyclopentene-4-
6 propylene radical, 1-methyl cyclopentene-4-propylene radical, 3-methyl
7 cyclopentene-4-propylene radical, 1,2-dimethyl cyclopentene-4-
8 propylene radical, 3,5-dimethyl cyclopentene-4-propylene radical,
9 1,3-dimethyl cyclopentene-4-propylene radical, 2,3-dimethyl
10 cyclopentene-4-propylene radical, 1,2,3-trimethyl cyclopentene-4-
11 propylene radical, and 1,2,3,5-tetramethyl cyclopentene-4-propylene
12 radical.

13 128. The process of claim 108, wherein the composition is a ethylene/methyl
14 acrylate/cyclohexenyl methyl acrylate terpolymer, a cyclohexenyl methyl
15 acrylate/ethylene copolymer, a cyclohexenyl methyl
16 methacrylate/styrene copolymer, a cyclohexenyl methyl acrylate
17 homopolymer or a methyl acrylate/cyclohexenyl methyl acrylate
18 copolymer.

-147-

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3 129. A non-odorous oxygen scavenging polymer composition comprising: (1)
 4 monomers derived from cyclic hydrocarbon moieties having at least one
 5 cyclic allylic or cyclic benzylic hydrogen and (2) a transition metal
 6 oxidation catalyst.

7

8 130. The composition of claim 129, wherein the composition comprises
 9 condensation polymers selected from the group consisting of polyesters,
 10 polyamides, polycarbonate, polyurethane, polyureas and polyether.

11

12

13 131. The composition of claim 129, wherein the cyclic allylic monomers are
 14 selected from the group consisting of structure (V), structure (VI) and
 15 structure (VII):

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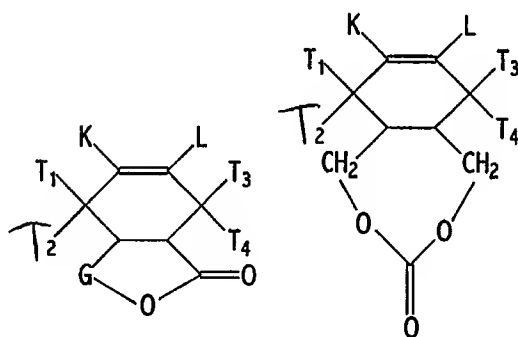
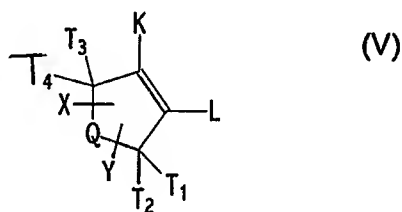
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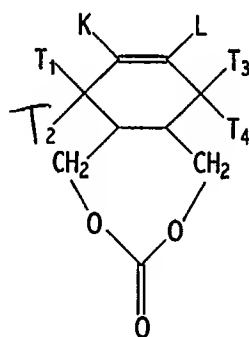
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(VI)

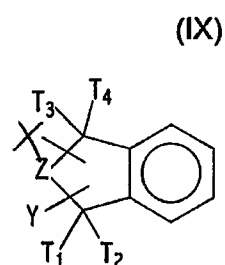
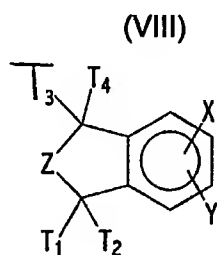


(VII)

-148-

1 with K, L, T₁, T₂, T₃, and T₄ being selected from the group consisting of
 2 -C_qH_{2q+1} with q being an integer in the range from 0 to 12 and wherein,
 3 when either K or L is -H, at least one of T₁, T₂, T₃ and T₄ is -H;
 4 and with X and Y being selected from the group consisting of -(CH₂)_n-
 5 OH, -(CH₂)_n-NH₂, -(CH₂)_nNC=O and -(CH₂)_m-(C=O)-A with n being an
 6 integer in the range from 1 to 12 and m being an integer in the range
 7 from 0 to 12 and A being selected from the group consisting of -OH,
 8 -OCH₃, -OC₂H₅, -OC₃H₇ and halides; and Q being selected from the
 9 group consisting of -(C_tH_{2t-2}) with t being an integer in the range from 1
 10 to 4;
 11 and with G being selected from -(C=O)- and -(C_nH_{2n+1})- with n being an
 12 integer from 0 to 12.

13
 14 132. The composition of claim 129, wherein the cyclic benzylic monomers are
 15 selected from the group consisting of structure (VIII), structure (IX), structure
 16 (X), structure (XI), structure (XII), and structure (XIII)



-149-

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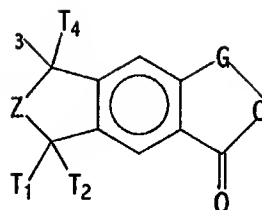
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(X)



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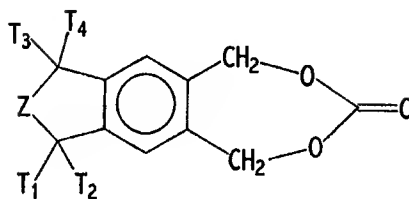
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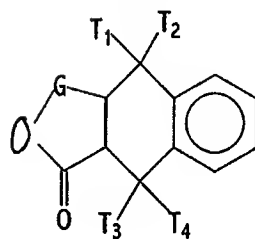
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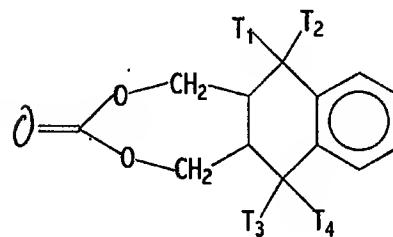
(XI)



(XII)



(XIII)



-150-

- 1 where X and Y are selected from the group consisting of $-(CH_2)_n-OH$,
 2 $-(CH_2)_n-NH_2$ and $-(CH_2)_m-(C=O)-R_1$ with n being an integer in the range
 3 from 1 to 12, and with m being an integer in the range from 0 to 12 and
 4 with R_1 being selected from the group consisting of $-OH$, $-OCH_3$,
 5 $-OC_2H_5$, $-OC_3H_7$ and halides;
 6 with T_1 , T_2 , T_3 , and T_4 being selected from the group consisting of
 7 $-C_qH_{2q+1}$ with q being an integer in the range from 0 to 12 and at least
 8 one of T_1 , T_2 , T_3 and T_4 being $-H$;
 9 and with X and Y being selected from the group consisting of –
 10 $(CH_2)_n-OH$, $-(CH_2)_n-NH_2$, $-(CH_2)_nNC=O$, and $-(CH_2)_m-(C=O)-A$ with n
 11 being an integer in the range from 1 to 12, and m being an integer in the
 12 range from 0 to 12 and A being selected from the group consisting of
 13 $-OH$, $-OCH_3$, $-OC_2H_5$, $-OC_3H_7$ and halides; and Z being selected from the
 14 group consisting of $-(C_tH_{2t-2})-$, $-O-$, $-NR_2-$, $-S-$, with t being an integer in
 15 the range from 1 to 4 and R_2 being selected from the group consisting of
 16 $-OH$, $-OCH_3$, $-OC_2H_5$, $-OC_3H_7$ and halides;
 17 and with G being selected from $-(C=O)-$ and $-(C_nH_{2n+1})-$ with n being an
 18 integer from 0 to 12.
- 19
- 20 133. The composition of claim 130, the composition being thermoplastic.
- 21
- 22 134. The composition of claim 130, the composition being thermoset.
- 23
- 24
- 25 135. The composition of claim 130, the composition being a multilayered
 26 structure with other layers being an aromatic polyester or copolyester
 27 selected from the group consisting of polyethylene terephthalate,
 28 polyethylene naphthalate, polypropylene terephthalate, polybutylene
 29 terephthalate, polyethylene isophthalate, polycyclohexanedimethanol

-151-

1 terephthalate, polybutylene naphthalate, polycyclohexanedimethanol
2 naphthalate, and copolymers and blends thereof.

3

4 136. The composition of claim 130, the composition being a multilayered
5 structure with other layers being polyamides or copolyamides selected from
6 the group consisting of Nylon 6, Nylon 66, Nylon 610 and mixtures thereof.

7

8

9 137. The composition of claim 130, the composition being a multilayered
10 structure with other layers being bisphenol A carbonate.

11

12 138. The composition of claim 130, the composition being a multilayered
13 structure with other layers being vinylic polymers or copolymers selected
14 from the group consisting of ethylene polymer, ethylene copolymer, propylene
15 polymer, propylene copolymer, styrene polymer, styrene copolymer, acrylate
16 polymer, acrylate copolymer, vinyl chloride polymer, vinyl chloride copolymer,
17 divinyl chloride polymer, divinyl chloride copolymer, fluorinated vinyl polymer,
18 fluorinated vinyl copolymer and mixtures thereof.

19

20

21 139. The composition of claim 130, the composition being blended with an
22 aromatic polyester or copolyester selected from the group consisting of
23 polyethylene terephthalate, polyethylene naphthalate, polypropylene
24 terephthalate, polybutylene terephthalate, polyethylene isophthalate,
25 polycyclohexanedimethanol terephthalate, polybutylene naphthalate,
26 polycyclohexanedimethanol naphthalate, and copolymers and blends thereof.

27

28 140. The composition of claim 130, the composition being blended with
29 polyamides or copolyamides selected from the group consisting of Nylon 6,
30 Nylon 66, Nylon 610 and mixtures thereof.

- 1 141. The composition of claim 130, the composition being blended with
2 bisphenol A polycarbonate.
3
- 4 142. The composition of claim 130, the composition being a blend comprising
5 vinylic polymers or copolymers selected from the group consisting of ethylene
6 polymer, ethylene copolymer, propylene polymer, propylene copolymer,
7 styrene polymer, styrene copolymer, acrylate polymer, acrylate copolymer,
8 vinyl chloride polymer, vinyl chloride copolymer, divinyl chloride polymer,
9 divinyl chloride copolymer, fluorinated vinyl polymer, fluorinated vinyl
10 copolymer and mixtures thereof.
11
12
- 13 143. The composition of claim 130, the composition being laminated or
14 adhering onto a substrate selected from the group consisting of paper, foil,
15 high temperature film, metallized film, polyamide films, ethylene vinyl alcohol
16 film, silica coated film, nylon/EVOH/nylon, oriented polypropylene, polyester
17 film, polyethylene, polypropylene, polyester, oriented polyethylene
18 terephthalate and cellophane.
19
- 20 144. The composition of claim 129, wherein the composition comprises a
21 vinyl polymer selected from the group consisting of ethylene polymer,
22 ethylene copolymer, propylene polymer, propylene copolymer, styrene
23 polymer, styrene copolymer and mixtures thereof.
24
25
- 26 145. A rigid container for food or beverage, the container being molded from
27 a resin comprising a non-odorous oxygen scavenging polymer composition,
28 the composition comprising (1) monomers derived from cyclic hydrocarbon
29 moieties having at least one cyclic allylic or cyclic benzylic hydrogen and (2) a
30 transition metal oxidation catalyst.

-153-

1 146. The rigid container of claim 145, wherein the composition comprises
2 condensation polymers selected from the group consisting of polyesters,
3 polyamides, polycarbonate, polyurethane, polyureas, polysulfones and
4 polyether.

5

6 147. The rigid container of claim 145, wherein the cyclic allylic monomers are
7 selected from the group consisting of structure (V), structure (VI) and
8 structure (VII):

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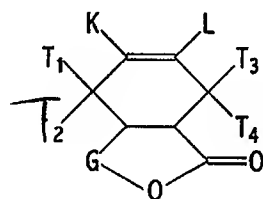
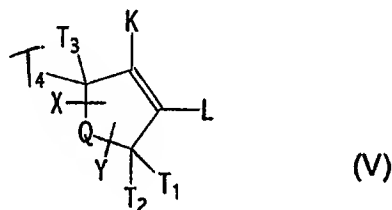
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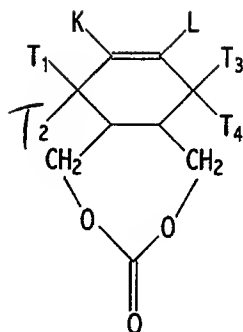
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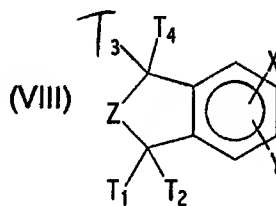
-154-



(VII)

with K, L, T₁, T₂, T₃, and T₄ being selected from the group consisting of -C_qH_{2q+1} with q being an integer in the range from 0 to 12 and wherein, when either K or L is -H, at least one of T₁, T₂, T₃ and T₄ is -H; and with X and Y being selected from the group consisting of -(CH₂)_n-OH, -(CH₂)_n-NH₂, -(CH₂)_nNC=O and -(CH₂)_m-(C=O)-A with n being an integer in the range from 1 to 12 and m being an integer in the range from 0 to 12 and A being selected from the group consisting of -OH, -OCH₃, -OC₂H₅, -OC₃H₇ and halides; and Q being selected from the group consisting of -(C_tH_{2t-2}) with t being an integer in the range from 1 to 4; and with G being selected from -(C=O)- and -(C_nH_{2n+1})- with n being an integer from 0 to 12.

148. The rigid container of claim 145, wherein the cyclic benzylic monomers are selected from the group consisting of structure (VIII), structure (IX), structure (X), structure (XI), structure (XII), and structure (XIII)



-155-

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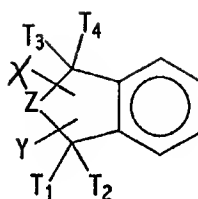
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(IX)

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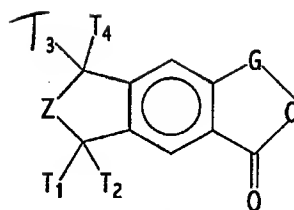
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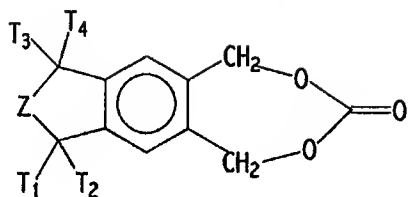
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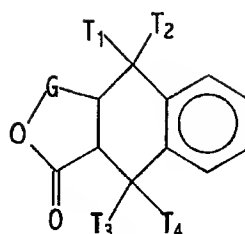
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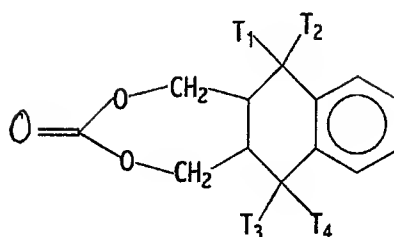


(XI)

-156-



(XII)



(XIII)

where X and Y are selected from the group consisting of $-(CH_2)_n-OH$, $-(CH_2)_n-NH_2$ and $-(CH_2)_m-(C=O)-R_1$ with n being an integer in the range from 1 to 12 and with m being an integer in the range from 0 to 12 and with R_1 being selected from the group consisting of $-OH$, $-OCH_3$, $-OC_2H_5$, $-OC_3H_7$ and halides;

with T_1 , T_2 , T_3 , and T_4 being selected from the group consisting of $-C_qH_{2q+1}$ with q being an integer in the range from 0 to 12 and at least one of T_1 , T_2 , T_3 and T_4 being $-H$;

and with X and Y being selected from the group consisting of $-(CH_2)_n-OH$, $-(CH_2)_n-NH_2$, $-(CH_2)_nNC=O$ and $-(CH_2)_m-(C=O)-A$ with n being an integer in the range from 1 to 12 and m being an integer in the range from 0 to 12 and A being selected from the group consisting of $-OH$, $-OCH_3$, $-OC_2H_5$, $-OC_3H_7$ and halides; and Z being selected from the group consisting of $-(C_tH_{2t-2})-$, $-O-$, $-NR_2-$, $-S-$, with t being an integer in

-157-

1 the range from 1 to 4 and R_2 being selected from the group consisting of
2 $-OH$, $-OCH_3$, $-OC_2H_5$, $-OC_3H_7$ and halides;
3 and with G being selected from $-(C=O)-$ and $-(C_nH_{2n+1})-$ with n being an
4 integer from 0 to 12.

5

6 149. The rigid container of claim 146, the composition being thermoplastic.

7 150. The rigid container of claim 146, the composition being thermoset.

8

9

10 151. The rigid container of claim 146, the composition being made by
11 coextrusion, blow molding or lamination with an aromatic polyester or
12 copolyester selected from the group consisting of polyethylene terephthalate,
13 polyethylene naphthalate, polypropylene terephthalate, polybutylene
14 terephthalate, polyethylene isophthalate, polycyclohexanedimethanol
15 terephthalate, polybutylene naphthalate, polycyclohexanedimethanol
16 naphthalate, and copolymers and blends thereof.

17

18 152. The rigid container of claim 146, the composition being made by
19 coextrusion, blow molding or lamination with polyamides or copolyamides
20 selected from the group consisting of Nylon 6, Nylon 66, Nylon 610 and
21 mixtures thereof.

22

23

24 153. The rigid container of claim 146, the composition being made by
25 coextrusion, blow molding or lamination with bisphenol A polycarbonate.

26

27 154. The rigid container of claim 146, the composition being made by
28 coextrusion, blow molding or lamination with vinylic polymers or copolymers
29 selected from the group consisting of ethylene polymer, ethylene copolymer,
30 propylene polymer, propylene copolymer, styrene polymer, styrene

-158-

1 copolymer, acrylate polymer, acrylate copolymer, vinyl chloride polymer, vinyl
2 chloride copolymer, divinyl chloride polymer, divinyl chloride copolymer,
3 fluorinated vinyl polymer, fluorinated vinyl copolymer and mixtures thereof.

4

5

6 155. The rigid container of claim 146, the composition being blended with
7 an aromatic polyester or copolyester selected from the group consisting of
8 polyethylene terephthalate, polyethylene naphthalate, polypropylene
9 terephthalate, polybutylene terephthalate, polyethylene isophthalate,
10 polycyclohexanedimethanol terephthalate, polybutylene naphthalate,
11 polycyclohexanedimethanol naphthalate, and copolymers and blends thereof.

12

13 156. The rigid container of claim 146, the composition being blended with
14 polyamides or copolyamides selected from the group consisting of Nylon 6,
15 Nylon 66, Nylon 610 and mixtures thereof.

16

17

18 157. The rigid container of claim 146, the composition being blended with
19 bisphenol A carbonate.

20

21 158. The rigid container of claim 146, the composition being blended with
22 vinylic polymers or copolymers selected from the group consisting of ethylene
23 polymer, ethylene copolymer, propylene polymer, propylene copolymer,
24 styrene polymer, styrene copolymer, acrylate polymer, acrylate copolymer,
25 vinyl chloride polymer, vinyl chloride copolymer, divinyl chloride polymer,
26 divinyl chloride copolymer, fluorinated vinyl polymer, fluorinated vinyl
27 copolymer and mixtures thereof.

28

29

-159-

- 1 159. The rigid container of claim 146, the composition being laminated or
2 adhering onto a substrate selected from the group consisting of paper, foil,
3 high temperature film, metallized film, polyamide films, ethylene vinyl alcohol
4 film, silica coated film, nylon/EVOH/nylon, oriented polypropylene, polyester
5 film, oriented polyethylene terephthalate, polypropylene, polyester, and
6 cellophane.
- 7 160. The rigid container of claim 146, wherein the composition comprises
8 a vinyl polymer selected from the group consisting of ethylene polymer,
9 ethylene copolymer, propylene polymer, propylene copolymer, styrene
10 polymer, styrene copolymer and mixtures thereof.
- 11
- 12 161. The rigid container according to claim 145, wherein the composition is
13 a single layer.
- 14
- 15
- 16 162. The rigid container according to claim 145, wherein the composition is
17 multilayered.
- 18
- 19 163. The rigid container according to claim 162, wherein the composition
20 comprises an outer air contact layer and an inner oxygen scavenging layer.
- 21
- 22
- 23 164. The rigid container according to claim 163, wherein the outer air
24 contact layer comprises an oxygen barrier resin selected from the group
25 consisting of polyethylene terephthalate, polyethylene naphthalate and a
26 mixture of polyethylene terephthalate and polyethylene naphthalate.
- 27
- 28 165. The rigid container according to claim 163, wherein the composition
29 further comprises at least one of an inner food contact layer, a tie layer, and a
30 tinted ultraviolet protection layer.

-160-

1

2

3 166. The rigid container according to claim 165, wherein the inner food
4 contact layer comprises an oxygen barrier resin selected from the group
5 consisting of polyethylene terephthalate, polyethylene naphthalate and a
6 mixture of polyethylene terephthalate and polyethylene naphthalate.

7

8 167. The rigid container of claim 145, wherein oxygen scavenging by the
9 non-odorous oxygen scavenging polymer composition is initiated by moisture
10 or actinic radiation.

11

12

13 168. The rigid container of claim 145, wherein the transition metal catalyst
14 is a metal salt.

15

16 169. The rigid container of claim 168, wherein the metal in the metal salt is
17 cobalt.

18

19

20 170. The rigid container of claim 169, wherein the metal salt is selected
21 from the group consisting of cobalt neodecanoate, cobalt 2-ethylhexanoate,
22 cobalt oleate and cobalt stearate.

23

24 171. The rigid container of claim 145, wherein the non-odorous oxygen
25 scavenging composition further comprises at least one triggering material to
26 enhance initiation of oxygen scavenging.

27

28

29 172. The rigid container of claim 171, wherein the triggering material is a
30 photoinitiator.

-161-

1

2 173. The rigid container of claim 172, wherein the photoinitiator has an
3 ultraviolet absorption window above 320 nm.

4 174. The rigid container of claim 172, wherein the container further comprises
5 a tinted ultraviolet protection layer located between the layer comprising the
6 non-odorous oxygen scavenging composition and the inside of the rigid
7 container.

8

9 175. The rigid container of claim 174, wherein the tinted layer is the food
10 contact layer.

11

12

13 176. The rigid container of claim 174, wherein the resin comprises
14 condensation polymers selected from the group consisting of polyesters,
15 polyamides, polyurethane, polyureas, polysulfones, polycarbonates and
16 polyether.

17

18 177. The rigid container of claim 174, wherein the cyclic allylic monomers
19 are selected from the group consisting of structure (V), structure (VI) and
20 structure (VII):

21

22

23

24

25

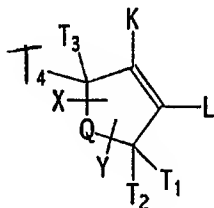
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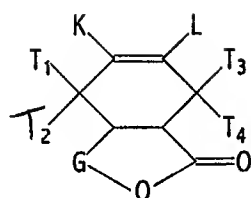
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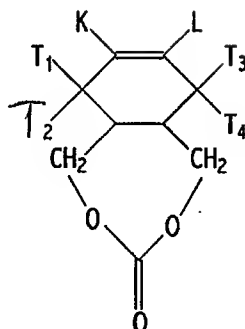


(V)

-162-



(VI)



(VII)

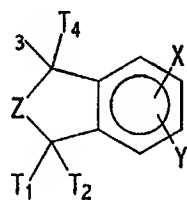
with K, L, T₁, T₂, T₃, and T₄ being selected from the group consisting of
 $-C_qH_{2q+1}$ with q being an integer in the range from 0 to 12 and wherein,
 when either K or L is -H, at least one of T₁, T₂, T₃ and T₄ is -H;
 and with X and Y being selected from the group consisting of
 $-(CH_2)_n-OH$, $-(CH_2)_n-NH_2$, $-(CH_2)_nNC=O$ and $-(CH_2)_m-(C=O)-A$ with n being
 an integer in the range from 1 to 12 and m being an integer in the range

-163-

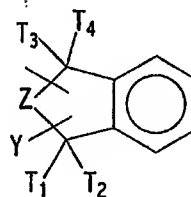
from 0 to 12 and A being selected from the group consisting of -OH, -OCH₃, -OC₂H₅, -OC₃H₇ and halides; and Q being selected from the group consisting of -(C_tH_{2t-2}) with t being an integer in the range from 1 to 4; and with G being selected from -(C=O)- and -(C_nH_{2n+1})- with n being an integer from 0 to 12.

178. The rigid container of claim 174, wherein the cyclic benzylic monomers are selected from the group consisting of structure (VIII), structure (IX), structure (X), structure (XI), structure (XII), and structure (XIII):

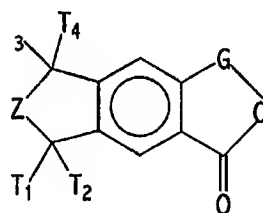
(VIII)



(IX)

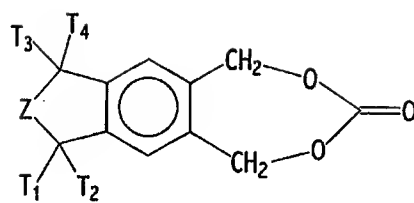


(X)



-164-

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(XI)

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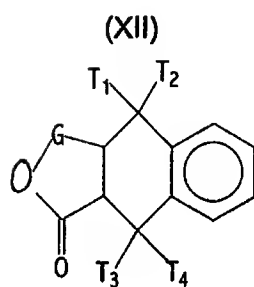
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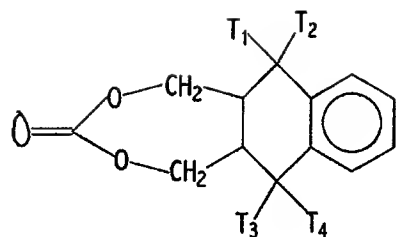
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22

23



(XIII)



24 where X and Y are selected from the group consisting of $-(CH_2)_n-OH$,
 25 $-(CH_2)_n-NH_2$ and $-(CH_2)_m-(C=O)-R_1$ with n being an integer in the range
 26 from 1 to 12 and with m being an integer in the range from 0 to 12 and

-165-

1 with R_1 being selected from the group consisting of -OH, -OCH₃, -OC₂H₅,
 2 -OC₃H₇ and halides;
 3 with T_1 , T_2 , T_3 , and T_4 being selected from the group consisting of
 4 -C_qH_{2q+1} with q being an integer in the range from 0 to 12 and at least
 5 one of T_1 , T_2 , T_3 and T_4 being -H;
 6 and with X and Y being selected from the group consisting of
 7 -(CH₂)_n-OH, -(CH₂)_n-NH₂, -(CH₂)_nNC=O and -(CH₂)_m-(C=O)-A with n
 8 being an integer in the range from 1 to 12 and m being an integer in the
 9 range from 0 to 12 and A being selected from the group consisting of
 10 -OH, -OCH₃, -OC₂H₅, -OC₃H₇ and halides; and Z being selected from the
 11 group consisting of -(C_tH_{2t-2})-, -O-, -NR₂-, -S-, with t being an integer in
 12 the range from 1 to 4 and R_2 being selected from the group consisting of
 13 -OH, -OCH₃, -OC₂H₅, -OC₃H₇ and halides;
 14 and with G being selected from -(C=O)- and -(C_nH_{2n+1})- with n being an
 15 integer from 0 to 12.

16
 17 179. The rigid container of claim 176, the composition being thermoplastic.

18
 19 180. The rigid container of claim 176, the composition being thermoset.

20
 21
 22 181. The rigid container of claim 176, the composition being in a multilayer
 23 structure with other layers, at least one of the other layers comprising an
 24 aromatic polyester or copolyester selected from the group consisting of
 25 polyethylene terephthalate, polyethylene naphthalate, polypropylene
 26 terephthalate, polybutylene terephthalate, polyethylene isophthalate,
 27 polycyclohexanedimethanol terephthalate, polybutylene naphthalate,
 28 polycyclohexanedimethanol naphthalate, and copolymers and blends
 29 thereof.

30

-166-

1 182. The rigid container of claim 176, the composition being in a multilayer
2 structure with other layers, at least one of the other layers comprising
3 polyamides or copolyamides selected from the group consisting of Nylon 6,
4 Nylon 66, Nylon 610 and mixtures thereof.

5
6 183. The rigid container of claim 176, the composition being in a multilayer
7 structure with other layers, at least one of the other layers comprising
8 bisphenol A carbonate.

9
10
11 184. The rigid container of claim 176, the composition being in a multilayer
12 structure with other layers, at least one of the other layers comprising vinyllic
13 polymers or copolymers selected from the group consisting of ethylene
14 polymer, ethylene copolymer, propylene polymer, propylene copolymer,
15 styrene polymer, styrene copolymer, acrylate polymer, acrylate copolymer,
16 vinyl chloride polymer, vinyl chloride copolymer, divinyl chloride polymer,
17 divinyl chloride copolymer, fluorinated vinyl polymer, fluorinated vinyl
18 copolymer and mixtures thereof.

19
20 185. The rigid container of claim 176, the composition being blended with an
21 aromatic polyester or copolyester selected from the group consisting of
22 polyethylene terephthalate, polyethylene naphthalate, polypropylene
23 terephthalate, polybutylene terephthalate, polyethylene isophthalate,
24 polycyclohexanedimethanol terephthalate, polybutylene naphthalate,
25 polycyclohexanedimethanol naphthalate, and copolymers and blends thereof.

26
27
28 186. The rigid container of claim 176, the composition being blended with
29 polyamides or copolyamides selected from the group consisting of Nylon 6,
30 Nylon 66, Nylon 610 and mixtures thereof.

-167-

1

2 187. The rigid container of claim 176, the composition being blended with
3 bisphenol A carbonate.

4

5

6 188. The rigid container of claim 176, the composition being blended with
7 vinylic polymers or copolymers selected from the group consisting of ethylene
8 polymer, ethylene copolymer, propylene polymer, propylene copolymer,
9 styrene polymer, styrene copolymer, acrylate polymer, acrylate copolymer,
10 vinyl chloride polymer, vinyl chloride copolymer, divinyl chloride polymer,
11 divinyl chloride copolymer, fluorinated vinyl polymer, fluorinated vinyl
12 copolymer and mixtures thereof.

13

14 189. The rigid container of claim 176, the composition being laminated or
15 adhering onto a substrate selected from the group consisting of paper, foil,
16 high temperature film, metallized film, polyamide films, ethylene vinyl alcohol
17 film, silica coated film, nylon/EVOH/nylon, oriented polypropylene, polyester
18 film, polyethylene, polypropylene, oriented polyethylene terephthalate, and
19 cellophane.

20

21

22 190. The rigid container of claim 176, wherein the composition comprises a
23 vinyl polymer selected from the group consisting of ethylene polymer,
24 ethylene copolymer, propylene polymer, propylene copolymer, styrene
25 polymer, styrene copolymer and mixtures thereof.

26 191. The rigid container according to claim 176, wherein the composition
27 comprises an outer air contact layer and an inner oxygen scavenging layer.

28

29 192. The rigid container according to claim 191, wherein the outer air contact
30 layer comprises an oxygen barrier resin selected from the group consisting of

-168-

1 polyethylene terephthalate, polyethylene naphthalate and a mixture of
2 polyethylene terephthalate and polyethylene naphthalate.

3

4

5 193. The rigid container according to claim 176, wherein the composition
6 further comprises at least one of an inner food contact layer, a tie layer, and a
7 tinted ultraviolet protection layer.

8

9 194. The rigid container according to claim 193, wherein the inner food
10 contact layer comprises an oxygen barrier resin selected from the group
11 consisting of polyethylene terephthalate, polyethylene naphthalate and a
12 mixture of polyethylene terephthalate and polyethylene naphthalate.

13

14

15 195. The rigid container of claim 176, wherein the transition metal catalyst is
16 a metal salt.

17

18 196. The rigid container of claim 195, wherein the metal in the metal salt is
19 cobalt.

20

21

22 197. The rigid container of claim 196, wherein the metal salt is selected from
23 the group consisting of cobalt neodecanoate, cobalt 2-ethylhexanoate, cobalt
24 oleate and cobalt stearate.

25 198. The rigid container of claim 197, wherein the triggering material is a
26 photoinitiator.

27

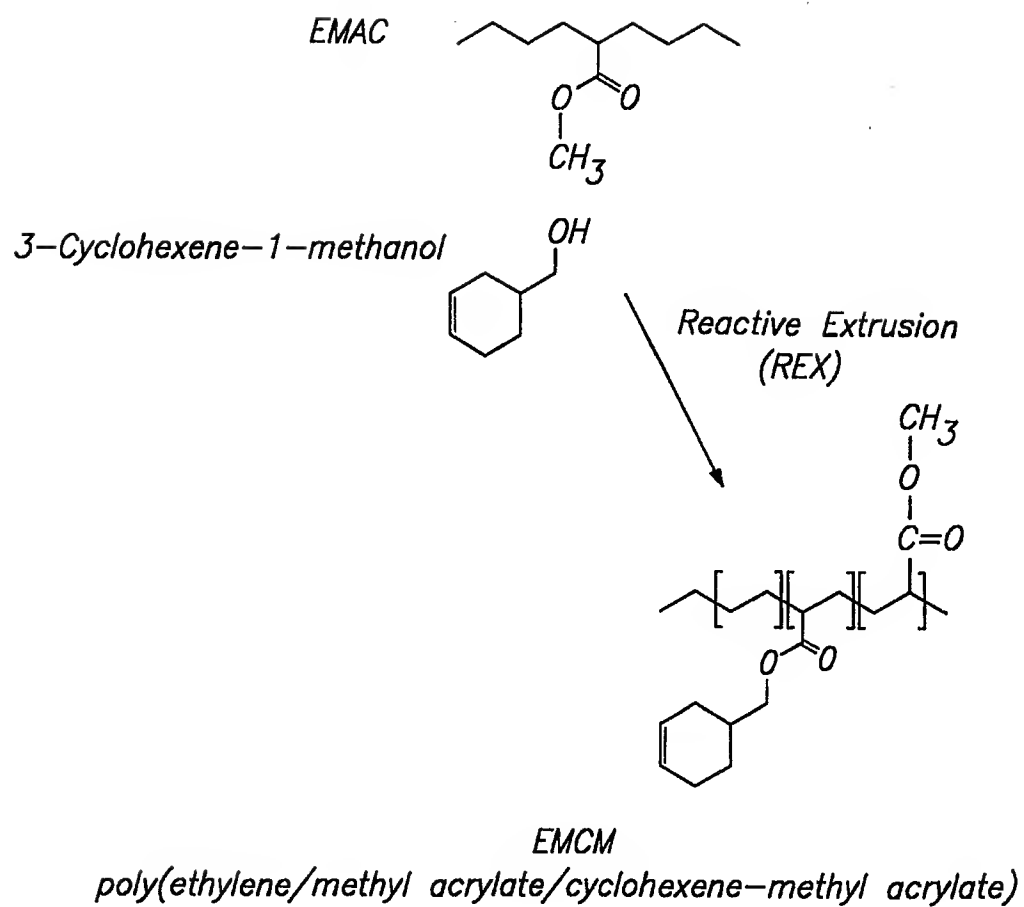
28 199. The rigid container of claim 198, wherein the photoinitiator has an
29 ultraviolet absorption window above 320 nm.

30

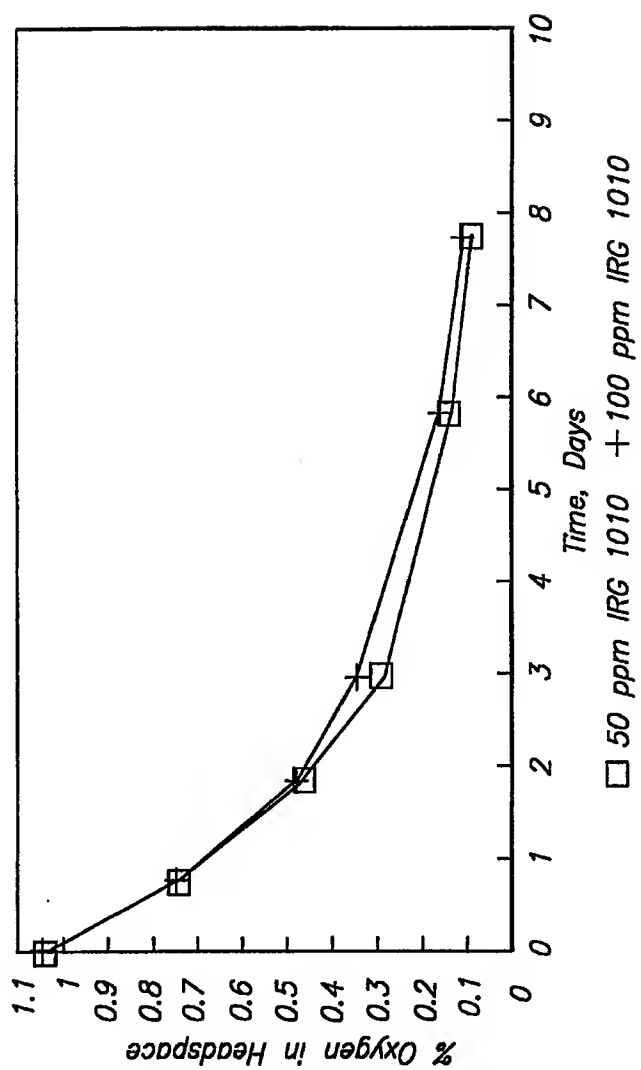
-169-

- 1
- 2 200. The rigid container of claim 145, wherein the rigid container is suitable
- 3 for packaging oxygen sensitive drinks for extended freshness and shelf life.
- 4
- 5 201. The rigid container of claim 200, wherein the oxygen sensitive drink is
- 6 beer.

1/5

**FIG. 1**

2/5

**FIG. 2**

3/5

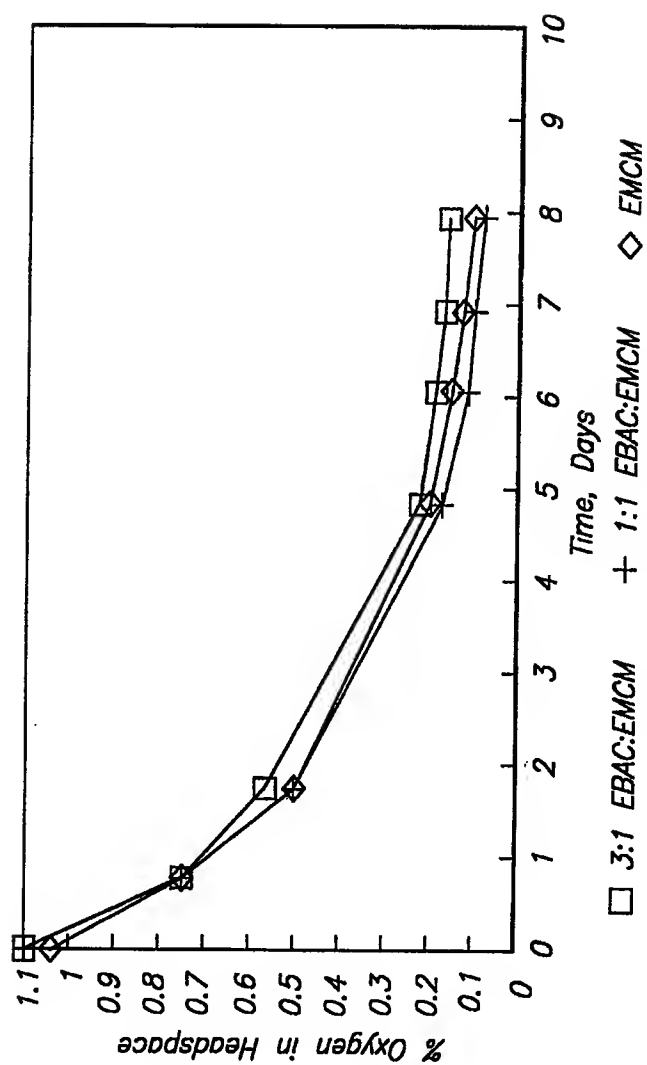


FIG. 3

4/5

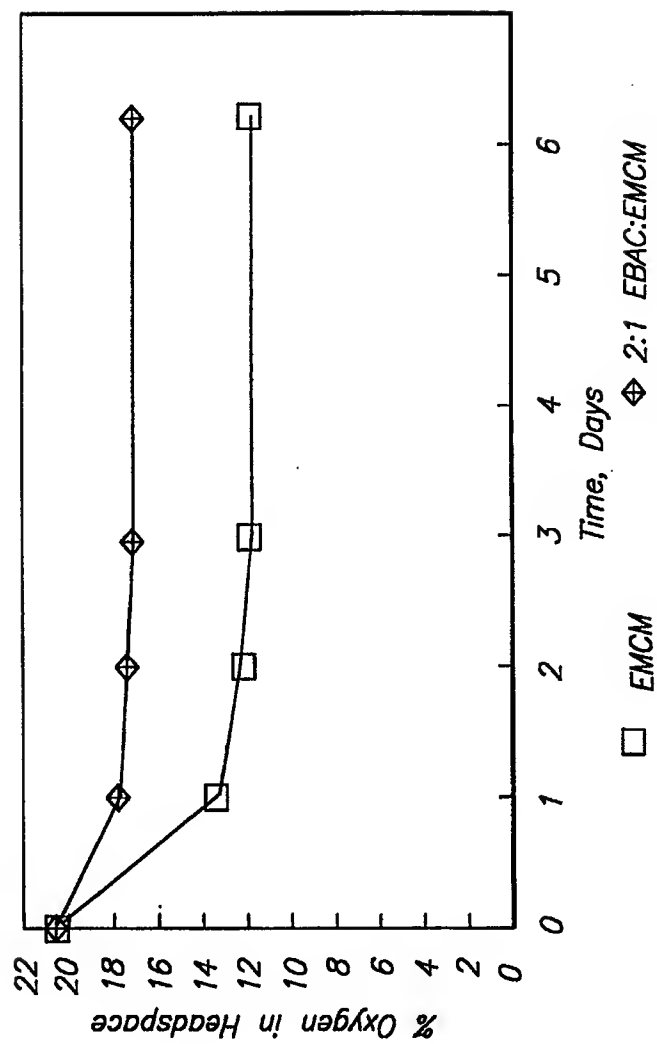
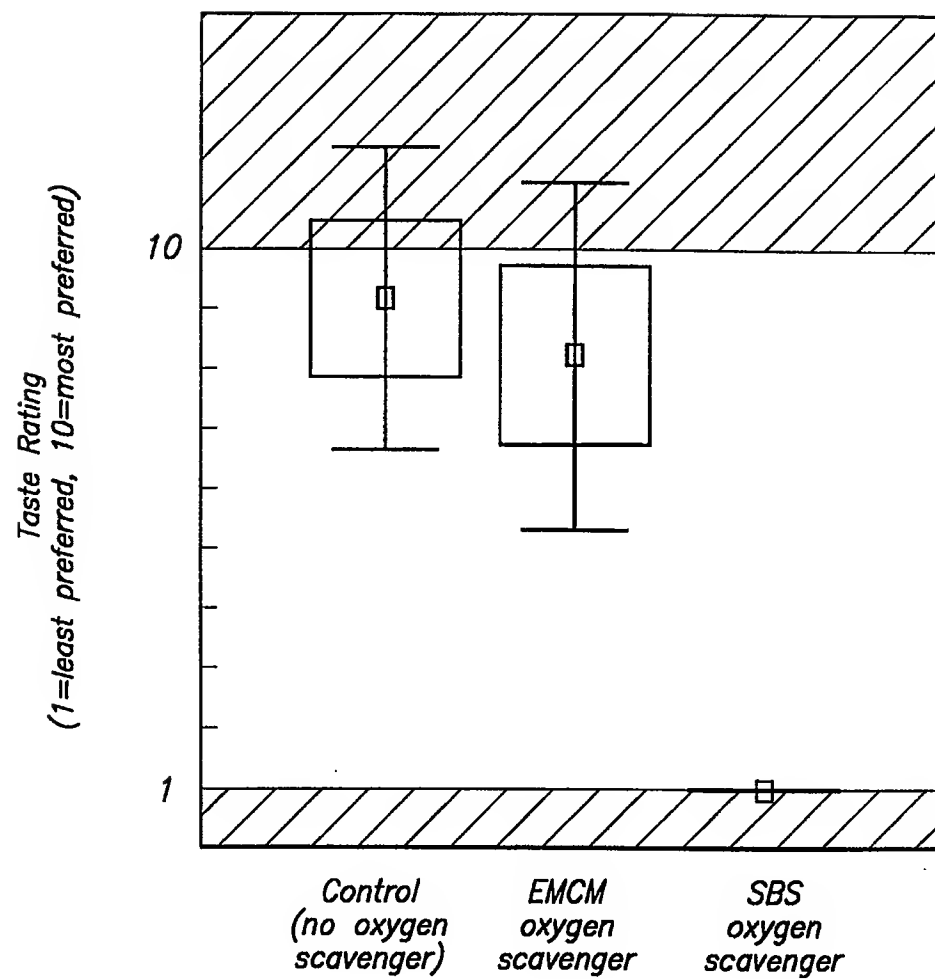


FIG. 4

5/5

**FIG. 5**